

B1.1 High pressure solution growth of GaN and related compounds

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A INTRODUCTION

Homoepitaxial growth of nitride layers on nitride single crystalline substrates is the best way to reduce the dislocation density in the active structures of GaN based optoelectronic devices. Unfortunately, bulk crystals of nitrides cannot be obtained by such established techniques as Czochralski or Bridgman growth from stoichiometric melts due to extremely high melting temperatures and very high decomposition pressures at melting (TABLE 1). Growth of semiconductor quality crystals with these conditions would be practically impossible. Therefore the crystals have to be grown by methods requiring lower temperatures. It will be shown that GaN single crystals with dimensions and properties sufficient for homoepitaxy can be grown from the solution in liquid gallium at high pressure of N₂ gas.

TABLE 1 Melting conditions for III-N compounds.

Nitride	T ^M , (K) _{theory}	p _{N₂} (kbar)
AlN	~3500 [1]	0.2 [3]
GaN	~2800 [1]	45 [4,5]
InN	~2200 [1,2]	60 [2]

B GAS PRESSURE REACTORS FOR CRYSTALLISATION

For the crystallisation of GaN, gas pressure chambers with volumes up to 1500 cm³ are used. The 3-zone cylindrical graphite furnace is placed inside the high pressure chamber and is immersed in pressurised nitrogen gas. The maximum pressure reaches 20 kbar and maximum temperature is 2000 K. The working volume of the furnace allows the use of crucibles containing up to 100 cm³ of liquid Ga. The crucibles are made from either graphite or hexagonal BN. In most cases, they are of cylindrical shape and can be used in both vertical and horizontal configurations.

The high pressure reactor is equipped with additional systems necessary for in situ annealing in vacuum, cooling of the pressure chamber and electronic stabilisation and programming of pressure and temperature. Pressure in the chamber is stabilised with a precision better than 10 bar. The temperature is measured by a set of thermocouples arranged along the furnace and coupled with the standard input power controllers. This allows stabilisation of the temperature to ± 0.2 degrees and programmable changes of temperature gradients in the crucible.

C THERMAL STABILITY OF AlN, GaN AND InN

FIGURE 1 shows the equilibrium p_{N₂} - T curves for AlN, GaN and InN. The curve for AlN was calculated by Slack and McNelly [6]. The one for GaN was determined by Karpinski and Porowski [5] based on gas pressure and Bridgman anvil experiments performed by Karpinski et al [4]. The curve for InN was obtained by Grzegory et al [7] and follows from differential thermal analysis (DTA) and annealing of InN at high N₂ pressure. The curves for GaN and InN deviate from linear dependence at

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higher pressures due to the non-ideal behaviour of N_2 gas. The diagrams indicate that at a pressure of 1 bar, AlN is thermodynamically stable up to temperatures approaching 3000 K; GaN is stable up to ~1200 K, whereas InN loses its stability at temperatures as low as ~600 K.

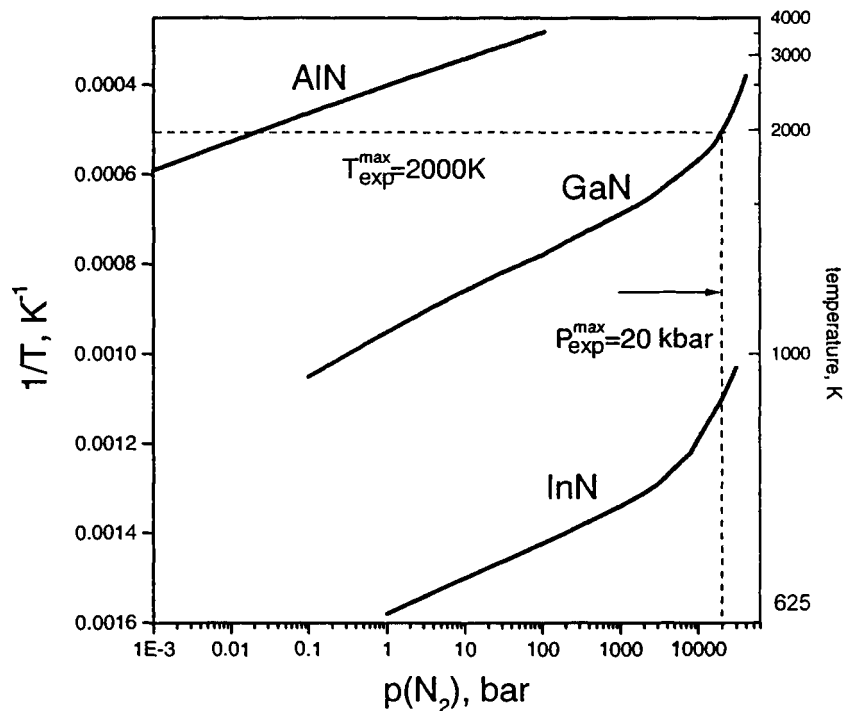


FIGURE 1 Equilibrium N_2 pressure over III-V nitrides.

As mentioned above, the gas pressure technique allows experiments at pressures up to 20 kbar and at temperatures up to about 2000 K. Therefore for AlN, the difficulty is not in attaining the necessary pressure, which is relatively low, but in attaining a sufficiently high temperature in order to achieve good nitrogen solubility in the melt. For InN, there is the equipment pressure limit of 20 kbar which determines the maximum temperature of InN stability. This is only ~900 K which is much lower than the expected melting point. For GaN, the maximum equilibrium temperature determined by a nitrogen pressure of 20 kbar is 1960 K, which comes closest to the melting temperature and suggests the best conditions for crystallisation.

D SOLUBILITY OF N IN LIQUID Al, Ga AND In

The melting temperatures of the nitrides (TABLE 1) are significantly higher than the maximum temperature available for each of the compounds in the gas pressure chamber. This causes a very low solubility of AlN, GaN and InN in the corresponding liquid metals.

The solubility of N in liquid Ga was experimentally determined [7,8] for the conditions corresponding to the equilibrium p_{N_2} - T curve. In the high pressure experimental system (20 kbar, 2000 K), the nitrogen content in Ga can be increased up to ~1 at.% which is sufficient for effective crystallisation from the solution.

Calculations [7,8] performed for AlN and InN suggest that the maximum nitrogen content in the solution for the Al-AlN system, determined by the technical limit for temperature (2000 K), is a few times lower than for GaN.

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For the In-InN system, the maximum concentration is determined by the available N₂ pressure (20 kbar) which limits the stability range of the nitride to $T < 900$ K. At such low temperatures, the expected concentration of N in liquid In is lower than 0.001 at. %.

E KINETIC LIMITATIONS OF DISSOLUTION OF N₂ IN LIQUID Al, Ga AND In

The first stage of nitride synthesis from its constituents is the dissolution of nitrogen in liquid metal. This process was analysed [9,10] by ab initio quantum mechanical calculations using the density functional theory (DFT) approximation [11-13].

An N₂ molecule approaching the metal surface is repelled by the surface by an effective potential barrier (FIGURE 2) [9,10]. If the energy of the N₂ molecule is sufficient to overcome the potential barrier the dissociation of the molecule and formation of bonds between nitrogen and metal atoms take place. The potential barriers are considerably lower than the bonding energy of the N₂ molecule. However, their values are quite high, which suggests that the dissociation process can be kinetically controlled even for relatively high temperatures. The barrier for Al is the lowest and for In is the highest. Therefore, the dissociation process and subsequent nitrogen dissolution will require higher temperatures for In than for Al (FIGURE 3).

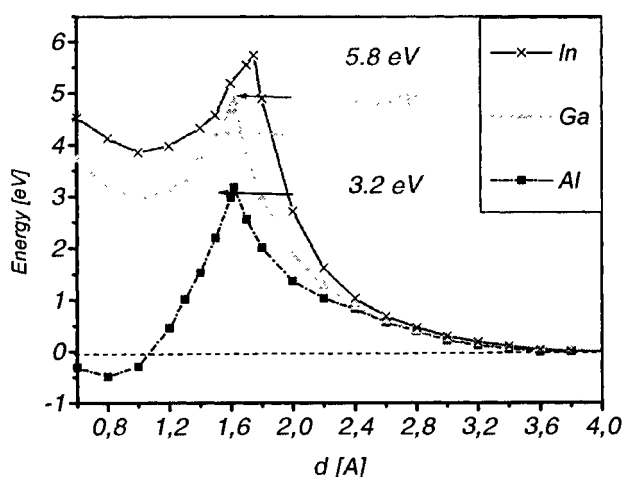


FIGURE 2 Energy of interaction of N₂ molecule with Al, Ga and In surfaces.

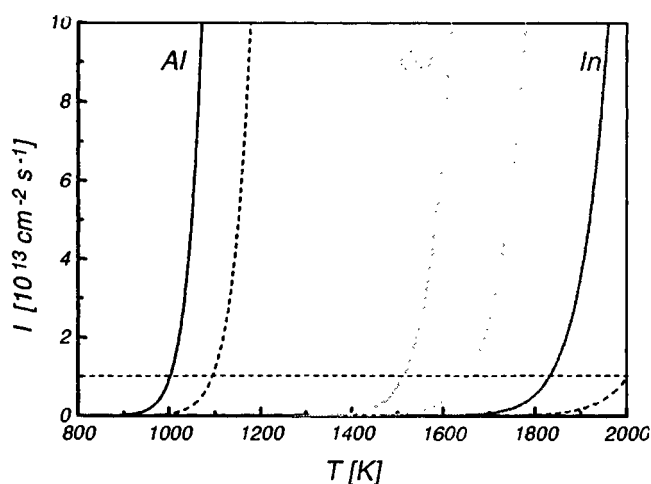


FIGURE 3 N₂ dissociation rate on Al, Ga and In surfaces.
Solid lines: $p = 20$ kbar; dashed lines: $p = 1$ kbar.

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The efficiency of the N_2 dissolution process at certain T and p was estimated from simple statistical evaluation of the stream of N_2 molecules that have higher energy than the corresponding barrier. FIGURE 3 shows the temperature dependence of the rate of dissociation for two pressures (1 kbar, 20 kbar). The dotted line of the diagram corresponds to the dissociation rate $I(T)$ which is so low that below this point the synthesis of $A^{III}N$ nitride is practically impossible. As a practical limit the efficiency of 10 mg of nitride for a 100 hr process per 1 cm^2 was used. The intersection of the dotted line with the calculated reaction rates therefore determines the lowest temperatures for direct synthesis of $A^{III}N$ nitrides from N_2 gas and liquid metal. For 20 kbar these temperatures are 1000 K, 1500 K and 1800 K for AlN, GaN and InN, respectively. These estimations are consistent with the experimental observation of combustion direct synthesis of AlN at 1300 K [14], crystallisation of GaN from the solution of N in liquid gallium at 1600 - 1900 K [15] and the absence of InN synthesis from its constituents up to 900 K [7]. The kinetic barrier for InN can probably be avoided by the use of InN powder as a source of nitrogen. However, as shown in Section D the estimated solubility of nitrogen in liquid indium is extremely small for temperatures below 900 K, which makes growth of the InN crystals from the solution in liquid indium practically impossible.

F HIGH N_2 PRESSURE SOLUTION GROWTH OF GaN

GaN crystals were grown from the solution in pure liquid gallium and in Ga alloyed with 0.2 - 0.5 at.% of Mg, Ca or Zn. The supersaturation in the growth solution is created by the application of a temperature gradient of 2 - 20°C/cm along the axis of the crucible. The nitrogen dissolves in the hotter end of the crucible and GaN crystallises in the cooler end. The slow cooling method was not applied due to small concentrations of nitrogen in the liquid gallium. The crystallisation experiments were performed without an intentional seeding and the crystals nucleated spontaneously on the crucible walls in the cooler zone of the solution. Typical duration of the process was 120 - 150 hours.

The GaN crystals grown by this method have wurtzite structure and they are mainly in the form of hexagonal platelets or hexagonal needles. High supersaturation favours growth in the c -direction which leads to needle-like forms.

Crystals in the form of hexagonal platelets grown slowly, with a rate $<0.1\text{ mm/hr}$, into $\{10\bar{1}0\}$ directions (perpendicular to the c -axis), are usually single crystals of perfect morphology suggesting stable layer-by-layer growth. They are transparent, with flat mirror-like faces. GaN platelets grown without intentional doping are shown in FIGURE 4. The growth is strongly anisotropic being much faster in directions perpendicular to the c -axis.

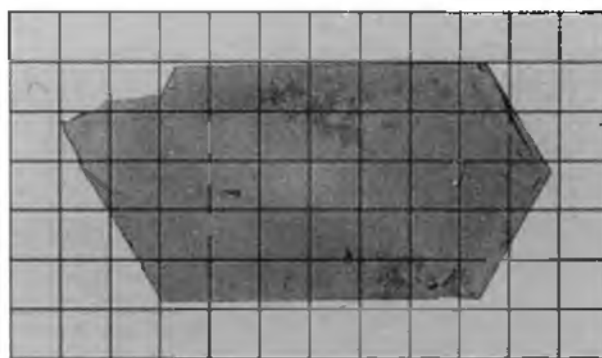


FIGURE 4 Typical GaN single crystal grown at high nitrogen pressure.
The distance between two grid lines corresponds to 1 mm.

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If the supersaturation is too high, edge nucleation on the hexagonal faces of GaN platelets is often observed, which is the first step to unstable growth on those faces. The tendency for unstable growth is stronger for one of the polar {0001} faces of the platelets. On this side, morphological features such as macrosteps, periodic inclusions of solute or cellular growth are observed. The opposite surface is always mirror-like and often atomically flat. Only this side of crystals grown from solutions in pure Ga can be etched by alkaline water solutions [16] and mechano-chemically polished. It was identified by X-ray photoelectron diffraction (XPD) measurements [17] as the (0001) N-terminated surface.

Crystals grown from solutions containing Mg, Ca or Zn also form hexagonal platelets similar to the undoped samples, but crystals containing Mg grow slightly more slowly in directions perpendicular to the c-axis and faster into c-directions, resulting in relatively smaller, but thicker, platelets.

G PHYSICAL PROPERTIES OF PRESSURE GROWN GaN CRYSTALS

GaN crystals grown from pure gallium solutions are highly conductive showing metallic behaviour (TABLE 2) in the temperature range 4.2 - 300 K. High free electron concentrations of $3 - 6 \times 10^{19} \text{ cm}^{-3}$ with mobilities of $30 - 90 \text{ cm}^2/\text{V s}$ [18] have been found. The main residual impurity detected in the crystals by SIMS [19] was oxygen at the estimated concentration of $10^{18} - 10^{19} \text{ cm}^{-3}$. It is well established that oxygen is a single donor in GaN. However, since the concentration of free electrons in the crystals is higher than the estimated concentration of the oxygen impurity, the presence of an additional donor cannot be excluded. The N-vacancy as the additional source of free electrons is often proposed [20,21].

TABLE 2 Electrical properties of pressure grown GaN crystals.

Crystal	Conductivity type	ρ ($\Omega \text{ cm}$, 300 K)	Carrier concentration (cm^{-3})
GaN	metallic	$10^{-3} - 10^{-2}$	$3 - 6 \times 10^{19}$, n-type
GaN:Mg	hopping	$10^4 - 10^6$	-

Following the theory [20,22], the most probable native defects in GaN crystals which are highly n-type are Ga-vacancies (V_{Ga}^{3-}). This is due to their low formation energy even under strongly Ga-rich conditions of crystallisation. The presence of negatively charged Ga vacancies at concentrations of 10^{18} cm^{-3} , in n-type pressure grown GaN crystals, was recently detected by positron annihilation experiments [23].

The introduction of 0.2 - 0.5 at.% of Ca or Zn into the growth solution does not change the character of electrical properties of the crystals, though the free electron concentration decreases by a factor of a few. In contrast, the addition of Mg into the growth solution drastically changes the electrical properties of GaN crystals increasing the resistivity by orders of magnitude (TABLE 2).

This increase of electrical resistivity in GaN:Mg crystals is related to a drastic decrease in free electron concentration. The temperature dependence of resistivity for these samples is typical for hopping conductivity [24] which suggests that the Fermi level lies within the gap. The optical absorption data [24] also indicate that the free carrier concentration in the Mg-doped GaN is very low. The free carrier absorption which dominates the low energy part of the absorption spectra for undoped GaN disappears completely for crystals grown from Mg-containing solutions.

In contrast to the conductive n-type crystals grown from pure Ga, no Ga-vacancies were detected by positron annihilation [25] in the highly resistive GaN:Mg crystals. This shows that the position of the Fermi level in GaN substantially modifies its stoichiometry, in qualitative agreement with the results of

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ab initio calculations [20,22] which predict the decrease of V_{Ga} concentration with decreasing Fermi energy.

Crystals grown from N solutions in pure Ga show strong yellow photoluminescence (PL) and a relatively weak PL signal close to the energy gap. Both signals disappear in crystals obtained from solutions doped with Mg, Zn and Ca. Instead, a strong broad PL occurs at energies 2.8 - 3.2 eV (at 80 K). For different samples doped with the same impurity, the maximum of the peak can shift by as much as 0.1 eV. The mechanism of this luminescence is not well understood.

The structure of the GaN crystals was investigated by X-ray diffraction methods [26]. For conductive crystals, the shape of the X-ray rocking curves ((0002)CuK α reflection) depends on the size of the crystal. The full widths at half maximum (FWHM) were 20 - 30 arcsec for 1 mm crystals and 30 - 40 arcsec for 1 - 3 mm ones. For larger platelets the rocking curves often split into a few ~30 - 40 arcsec peaks showing a presence of low angle (1 - 3 arcmin) boundaries separating grains of 0.5 - 2 mm in size. Misorientation between grains increases monotonically from one end of the crystal to the other.

TEM examination of GaN crystals by Liliental-Weber et al [27] determined that one of the polar surfaces of high pressure solution-grown GaN crystals (especially for the smaller ones) is often atomically flat (2 - 3 monolayer step heights present) and that the crystal under this surface is practically free of extended defects. On the opposite surface, a number of extended defects like stacking faults, dislocation loops and Ga microprecipitates were observed. The relative thickness of the defect-containing part usually consists of 10% of the entire thickness of the platelet.

The lattice constants for undoped GaN and the highly conductive Ga:Zn and GaN:Ca bulk crystals vary slightly for different crystals as well as for different areas of the individual crystals [26,28]. This is caused by the differences in free electron concentration and can lead to certain strains in the crystals. For the Mg-doped crystals, there are no free electrons and therefore the lattice parameters are uniform for individual crystals and the same for different samples [28]. Elimination of the strains in the GaN:Mg crystals is the reason for the improvement of their structure. The rocking curves are narrower and no low angle boundaries are observed even for 8 mm single crystalline GaN:Mg platelets. The strains in the undoped GaN crystals are extremely small (<0.02%) but their presence can adequately explain the wider rocking curves than for the Mg-doped samples.

Comparative studies of diffusion of Zn into heteroepitaxial GaN layers on sapphire and bulk pressure grown crystals showed that dislocations play a very important role in the diffusion process in heteroepitaxial GaN layers [29]. The penetration of Zn into bulk crystal is a few orders of magnitude slower than into the heteroepitaxial layer. A similar effect of reduced diffusion due to the reduced density of dislocations can be expected for homoepitaxial GaN layers. Consequently this can improve the quality of GaN p-n junctions.

H SYNTHESIS AND CRYSTALLISATION OF AlN AND InN

The rate of AlN synthesis from constituents at high nitrogen pressure is very high. A thermal explosion was observed during heating of a bulk Al sample in N₂ gas, at pressures of 0.1 - 6.5 kbar [14]. The combustion product is AlN powder or ceramic. At pressures higher than 6.5 kbar, due to the increasing thermal conductivity of gas the synthesis reaction is inhibited, and the metal can be heated up to the temperature of crystallisation. Due to low nitrogen solubility in Al, the crystallisation rate of AlN, at 1600 - 1800°C, is rather low (<0.02 mm/hr). The biggest AlN crystals (4 mm needles) have been obtained at 6.5 kbar where combustion occurred in part of the sample.

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For InN [2], due to kinetic and thermodynamical barriers crystal growth experiments resulted in very small crystallites (5 - 50 μm) grown by slow cooling of the system from the temperatures exceeding the stability limit for InN.

I CONCLUSION

High nitrogen pressure allows the extension of the stability range of AlN, GaN and InN for higher temperatures. This allows direct synthesis of GaN and AlN. However the thermodynamic and kinetic barriers prevent synthesis of InN using nitrogen pressures up to 20 kbar.

High quality GaN crystals were grown from solutions of atomic nitrogen in liquid Ga at N_2 pressures up to 20 kbar. Growth of AlN crystals requires higher temperatures to increase the solubility of N in the liquid Al. For InN a pressure of 20 kbar is not sufficient for effective crystallisation.

GaN crystals of both low and high electric conductivity can be grown under high pressure of nitrogen. Routinely grown GaN single crystals in a form of hexagonal platelets with surface area 60 - 100 cm^2 and dislocation densities lower than 10^5 cm^{-2} can be used as substrates for homoepitaxy.

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B1.2 Sublimation growth of GaN and AlN

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A INTRODUCTION

One of the methods of growing bulk GaN is a sublimation method [1-3]. In this method, the source GaN powder and a seed crystal or a substrate facing the source are loaded in a crucible. Upon heating the crucible, the source powder sublimates and recrystallises onto the seed crystal or on the substrate. When a system needs a reaction gas such as NH_3 for growth, the system is not a sublimation but a VPE system. Now, a 4-inch SiC wafer grown by a sublimation method is commercially available [4].

In this Datareview, bulk growth of GaN and AlN by a sublimation method and of GaN by a sublimation sandwich method is described. The source powder was analysed. The bulk GaN obtained was characterised by XRD (X-ray diffraction), TEM (transmission electron microscopy), and so on.

B CRYSTAL GROWTH OF GaN BY SUBLIMATION METHOD

GaN crystal growth by sublimation was first reported in the 1970s. Ejdar grew GaN using metal Ga, N_2 and NH_3 [5]. The crystals obtained after 0.5 - 12 hr of growth were whiskers a few millimetres long and 1 - 5 μm in diameter, needles a few millimetres long and half a millimetre thick, platelets 0.1 - 20 μm thick and prisms. Zetterstrom reported colourless hexagonal crystal needles of GaN with the largest size of 5 mm long and 1 mm thick after 72 hr of growth [6]. These crystals, however, were not large enough to be used as substrates, and the shape of the crystals was not controlled.

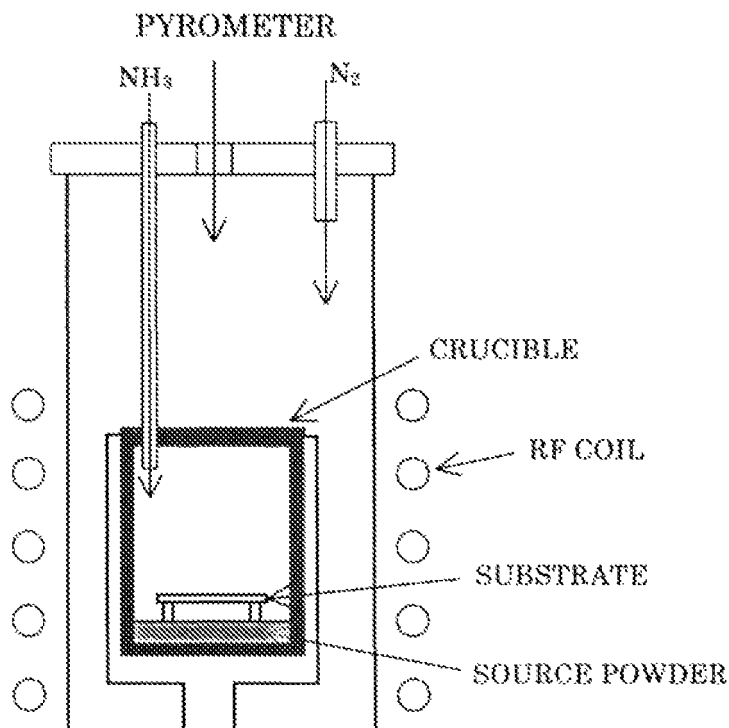


FIGURE 1 System used in the sublimation method.