Results of TDLS application for ammonia monitoring in a process of high-purity arsine and phosphine production

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Abstract Using the TDLS method it has been found that ammonia (NH_3) is the main impurity in arsine (AsH_3) and phosphine (PH_3), produced by hydrolysis of magnesium arsinide and phosphinide, respectively. NH_3 behavior is abnormal in solutions of these hydrides: NH_3 reveals the properties of a more volatile impurity in relation to arsine and phosphine, although its boiling temperature is higher than that of AsH_3 and PH_3. The observable anomaly is connected with the fact that in solutions of arsine and phosphine NH_3 shows properties differing from the properties of pure ammonia. It was supposed that the influence of intermolecular interaction between ammonia molecules, when diluted by arsine or phosphine, decreases. During the purification of arsine or phosphine one must continuously monitor the NH_3 concentration in the extraction of the light fraction in order to define the point at which to terminate the purification process.

1 Introduction

High-purity hydrates such as arsine (AsH_3) and phosphine (PH_3) are used for the production of epitaxial layers in A_3B_5 semiconductors. The quality of semiconductors manufactured depends on the presence of impurities [1]. Most important, from the point of view of the quality of the epitax-

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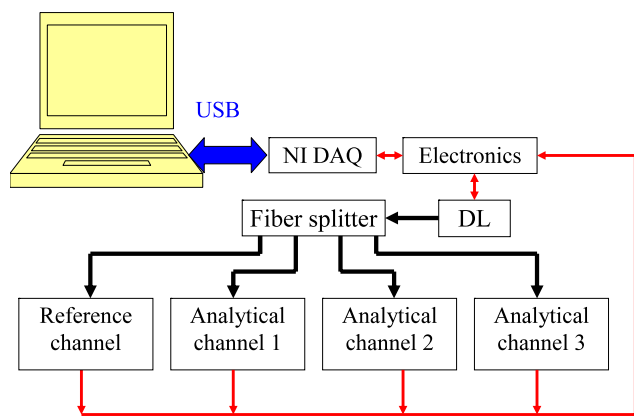e-mail: anber@nsc.gpi.ru

ial layers, is the presence of volatile inorganic hydrides of IV and VI group elements. Germane, silane and hydrogen sulphide are used for intentional doping of epitaxial A_3B_5 layers in CVD processes by n-type impurities. To achieve a current carrier concentration below 10^{15} cm^{-3}, the impurity concentration in hydrides has to be below 10 ppb.

The impurity content of hydrides is formed during their synthesis [2–4]. A universal method for the synthesis of volatile inorganic hydrides, including arsine and phosphine, is acid hydrolysis from an alloy of the hydride generating element with magnesium (either aluminium, or zinc):

$$Mg_3P_2 + 6HCl \rightarrow 2PH_3 + 3MgCl_2 \tag{1}$$

This method is used in the industrial production of arsine and phospine. The universality of this method of synthesis presents a potential danger of pollution of arsine and phosphine by other hydrides, including ammonia.

The above method was used for the synthesis of phospine, while for arsine synthesis a more selective method based on arsenic trichlorine reduction by sodium boron hydride was applied:

$$AsCl_3 + 3NaBH_4 + 9H_2O \rightarrow AsH_3 + 3NaCl + 3H_3BO_3$$
$$+ 9H_2 \tag{2}$$
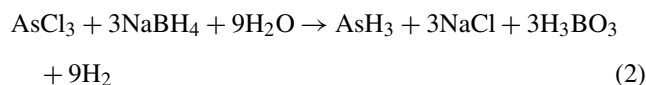
Existing techniques for the analysis of volatile hydrides during the synthesis of other hydrides by gas chromatography (see, for example, [5]) are time consuming and do not allow for the conduction of real time multichannel monitoring of the purification processing. Therefore, working out new, more sensitive and convenient techniques is a current and very important task.

Preliminary studies showed that the presence of ammonia in arsine at a 3–5% level influences the electrophysical para-

Fig. 1 Block-diagram of experimental set-up. *Black solid lines* correspond to optical fiber connections, narrower *red lines* to electrical connections

meters of the GaAs epitaxial layers: layers with p-type conductivity and with a carrier concentration of 4×10^{16} cm^{-3} and a mobility of 100 cm^2/V s at 77 K were obtained. Since the presence of ammonia in the other hydrates is important, it stipulates the purpose of this work: investigation of the possibility of applying TDLS to the monitoring of the behavior of ammonia impurities in arsine and phosphine in the course of their synthesis and purification.

2 Experimental set-up

The block-diagram of the experimental set-up is shown on Fig. 1. This diagram is similar to the one employed in [6] except for the fact that a multiple analytic channel system was used. This scheme allowed for the simultaneous detection of ammonia in the lower, middle and upper part of the purification column.

2.1 Diode laser

The NEL DFB 503074 (1.512 μm) pigtailed diode laser produced by NTT Electronics company [7] was used as the spectroscopic source for the instrument.

2.2 Electronics

The ammonia concentration measurements were performed by the well-known diode laser frequency scanning method (see, for example, [8]). In this method the initial scanning uses a diode laser, whose frequency was kept close to the absorption line by fine temperature tuning. Acquisition of the selected absorption line was accomplished by varying the DL current excitation. The diode laser was excited by current pulses of a trapezoidal waveform, allowing for DL frequency scanning.

Operation of the diode laser was performed using a NI 16-bit USB-6215 NI (250 kHz sample rate) electronic board instead of a 12-bit card, used in previous experiments. Two DAC (digital-to-analogue converters) of this board were used for generation of the DL current pulses and temperature control. Five ADC (analogue-to-digital converters) acquired signals from the temperature sensor, and from three analytical and one reference photodetectors (PD). Three additional ADC acquired signals, proportional to the pressure in the analytic cells. The device operation was controlled by a specialized program written in LabVIEW-8. This program performed signal processing (subtraction of the slope and the pedestal caused by the change in the laser intensity), low-pass filtering, averaging and concentration calculation.

The concentration was determined using the correlation function F_A for one of the analytic channels and the self-correlation function F_R for the reference channel:

$$F_A(\tau) = \int_0^T f_A(t+\tau) f_R(t)\, dt \tag{3}$$

$$F_R(\tau) = \int_0^T f_R(t+\tau) f_R(t)\, dt \tag{4}$$

Here f_A is the time-dependent signal in the analytic channel, f_R the time-dependent signal in the reference channel, T the pulse duration. Using the linear relationship

$$F_A = a F_R + b \tag{5}$$

The coefficients a and b were found by standard fitting. The concentration of ammonia in the analytic channel C_A could be found from the simple proportion

$$C_A = a \frac{L_R}{L_A} C_R \tag{6}$$

here C_R is for the concentrations in the reference channel, L_A and L_R are the optical paths in corresponding cells. Determination of the concentration with the help of correlation function serves as a filter since it takes into account only signals with the special waveform (the one in the reference channel). In order to get the correct concentration values the line waveform in the analytic channel should be the same or at least be close to the one in the reference channel.

2.3 Optical scheme

The DL output radiation was collimated within optical fibers and was divided into four channels with the help of two beam splitters: one divided radiation into reference and joint analytic channel in a proportion approximately 1:10 and the second split the joint analytic radiation into three analytic channels. In the analytic channels one-pass cells with different lengths (3, 5, 70 and 140 cm) were used. In short cells

Fig. 2 Ammonia absorption lines near 1.51 μm: *black curve*—at the pressure 1.6 Torr, *blue curve*—1.6 Torr in nitrogen at atmospheric pressure. *Red line*—absorption of 7 Torr of water. The optical path in all cases was 200 cm
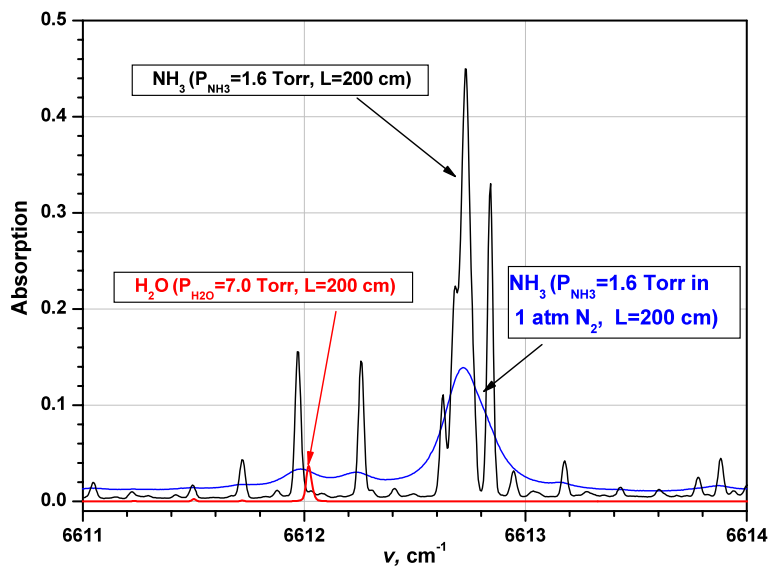
radiation was directly sent to a detector located at the opposite side of a cell; for long cells this was performed with a help of a collimator.

The analytical cells were made of electro-polished stainless steel tubes with quartz glass windows at their ends. The gas samples in the analytical cells were kept at lowered pressures. The pressure of ammonia in the reference cell, the sealed molybdenum glass tube of 30 mm long, was kept at the pressure of 50 Torr.

2.4 Experimental

The spectra of ammonia were recorded within the DL temperature tuning range and a group of absorption lines at 6612.7 cm^{-1} (1.512 μm) was chosen for the detection (Fig. 2). These absorption lines were tested in order to find out if they might overlap with absorption lines of the other molecules present in the investigated system, first of all with arsine, phosphine, carbon dioxide and water. It was found that arsine, phosphine and carbon dioxide did not absorb in this region and water has a weak absorption line ($\nu_1 + 2\nu_2$ band, transition 4_{41}–5_{50}, wavenumber 6612.018 cm^{-1} according to HITRAN database [9, 10]), shown by a red arrow on Fig. 2. This line is rather far from the ammonia absorption line chosen for detection. This situation was also analyzed in [11] and it was shown that the influence of this water line on ammonia detection is small, even at high water pressures.

This ammonia group of lines are resolved only at very low pressures, less than 10 Torr. At higher pressures this group of lines behaved as one line, as can be seen from Figs. 2 and 3.

Figure 3 shows the detected signals in the reference channel. The higher curve presents the signal, obtained with a Fabry-Pérot interferometer. This interferometer comprises a
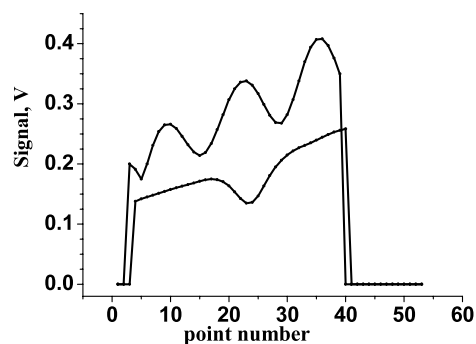

Fig. 3 Detected signals in reference channel: *higher curve*—etalon fringes in Fabry-Pérot interferometer (10 mm ZnSe plate), *lower curve*—reference cell 30 mm long with 50 Torr of ammonia

plane-parallel plate of ZnSe ($n = 2.43$, 10 mm thickness) having a free dispersion range of 0.206 cm. Taking that into account, the range of whole DL current scan can be calculated (0.6 cm^{-1}). The lower curve represents the signal, recorded with the reference cell. Having a calibrated abscissa scale (in cm^{-1}), it is possible to find the pressure dependencies of the line width (FWHM, full width at half maximum) and line shift. This was done for pure ammonia by fitting a Lorentz function (in Origin 8), and the results are presented in Fig. 4. At pressures higher than 300 Torr the absorption was too high and the line became too broad and fitting was incorrect. As can be seen, there is a strong nonlinear dependence of the line width and line shift upon pressure, and for correct detecting of ammonia with the help of a reference correlation function it is necessary to keep the pressure in the analytic cells low and close to that in the reference channel.

Experimentally, however, it was not convenient to keep the pressure in the cells so low and stable since the gas samples have to be changed often. So the calibration curve of the
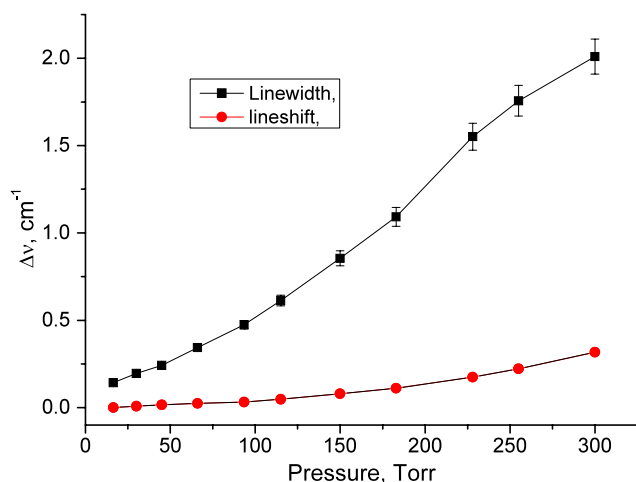
Fig. 4 Pressure dependence of the line width and line shift for the pure ammonia 1.512 μm absorption line

Table 1 Contents of ammonia in arsine and phosphine, synthesized by different methods

	Arsine		Phosphine
	From AsCl$_3$	From Mg$_3$As$_2$	from Mg$_3$P$_2$
Raw material	<0.005%	~0.05%	~0.05%
Light fractions	<0.005%	0.5–5%	0.5–5%

In the balloons with the light fractions, in which more volatile components than arsine and phosphine are concentrated in the process of arsine and phosphine purification, a high content of NH$_3$ was observed: up to tens of percent in arsine and up to the units of percent in phosphine. In the balloons with the heavy fractions, in which less volatile impurities are concentrated, ammonia was not detected.

The measured ammonia concentration in the light fraction is in contradiction with to the physical properties of ammonia, arsine and phosphine. The boiling point of ammonia (−33°C) is considerably higher than that of arsine (−62°C) and phosphine (−85°C). From this point of view ammonia had to concentrate in the heavy fractions of arsine or phosphine and should be absent in the light fractions. Table 1 shows that it is not so.

Arsine and phosphine have a critical temperature higher than room temperature and are kept in the balloons in the form of two-phase equilibrium system - liquid and gas phase. The measurements of the ammonia content in the gas and liquid phase of arsine and phosphine showed that ammonia has a higher content in the gas phase (Table 2).

Using data of ammonia concentrations in gas and liquid phase, the dependence of ammonia concentration in gas phase versus its concentration in liquid phase was plotted. The concentrations in the gas phase were measured when a balloon was in normal position, from the valve on its top. The concentrations in the liquid phase were measured when a balloon was turned upside-down. A small portion of liquid taken from the same valve in upside-down position was fully evaporated and the concentration was measured in this gas phase. The results are given in Fig. 5 along with the Raoult's law prediction [13] for an ideal gas. The saturation pressures, required for the calculation of the Raoult's law dependence, were taken at 8 and 14 atm for ammonia and arsine, respectively. The deviations of the experimental results from an ideal gas model are clearly seen.

Ammonia has the lowest saturated vapor pressure in comparison with arsine and phosphine, including that at room temperature. Based on this, ammonia in the balloon with arsine and phosphine should be concentrated in the liquid phase. The observed anomaly is connected with the fact that in the solutions of arsine and phosphine NH$_3$ reveals properties different from the properties of pure ammonia. In the solution the effect of intermolecular interaction between the molecules of ammonia apparently decreases.

concentration upon pressure dependence was experimentally measured and these data were used to find the ammonia concentration at pressures less than 300 Torr. The pressures in the cells were measured independently and were recorded as a function of time along with other parameters.

3 Results and discussion

The basic method of arsine and phosphine purification is the method of low-temperature distillation. For the purification the column with the middle reservoir was used. In the column there were three monitoring points: in the upper, lower and in the middle part of the purification column, the content of ammonia was monitored by the TDLS method (with the aid of the one-pass cells of different length). Parallel gas samples were taken into the gas chromatograph ("Tzvet-800", thermoconductivity detector), or into the cell of a Fourier spectrometer (Bruker "Tenzor-27", cell length 20 cm, resolution 1 cm^{-1}).

First the gases, contained in balloons with raw materials and in balloons obtained after the purification process, were analyzed. Ammonia was not found in arsine, obtained by the reduction of trichlorine arsenic by sodium boron hydride (2), which confirmed the selectivity of this method of synthesis. At the same time, NH$_3$ was present in arsine and phosphine, synthesized by the universal method - the hydrolysis of magnesium arsenide or phosphide (1). The source of ammonia is, most probably, magnesium nitride, which is formed as a result of interaction of magnesium with atmospheric nitrogen while producing magnesium arsenide or phosphide [12]. The content of ammonia in synthesized hydrides depends on the conditions of synthesis and initial raw material. In phosphine it reaches a value 0.05%, while in arsine the values are of order of 1%.

Table 2 Contents of ammonia in the gas and liquid phases in the balloons with arsine and phosphine

Hydride	Balloon number (volume, l)	NH$_3$ content, % vol		
		in gas phase, Cg	in liquid phase, Cl	Cg/Cl
AsH$_3$ from As$_2$Mg$_3$	075(2)	15.5	6.2	2.5
	0011(4)	17.1	7.6	2.3
PH$_3$ from P$_2$Mg$_3$	058(4)	0.043	0.030	1.4
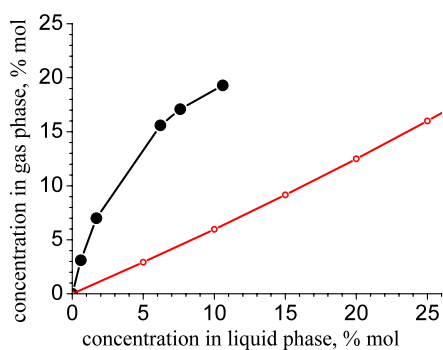
Fig. 5 Ammonia concentration in gas phase vs. its concentration in liquid phase. *Red line*: Raoult's law for ideal gas
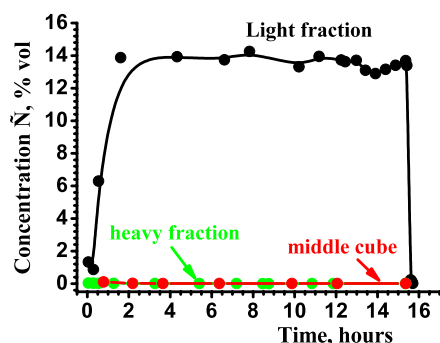
Fig. 6 Time dependence of HN$_3$ concentration measured in three TDLS channels during the distillation process

The time dependencies of ammonia content in different parts of the distillation column were also analyzed. Figure 6 shows the behavior of the ammonia concentration in the arsine purification process. In the course of purification an increase of ammonia concentration to the value of ∼14 vol.% was observed in the upper part and it remained constant for the 16 hours of purification. Simultaneously the contents of ammonia in the heavy fraction and in the middle cube were monitored. In the lower and in the middle parts of the distillation column, the ammonia concentration was below the detection limit (0.01%).

The experimental results again confirmed that in the solution of arsine ammonia behaves anomalously. It is concentrated in the light fraction; in this case its apparent boiling point is lower than in arsine, i.e., lower, than −62°C.

The arsine and phosphine purification processes were carried out with continuous monitoring of the NH$_3$ content
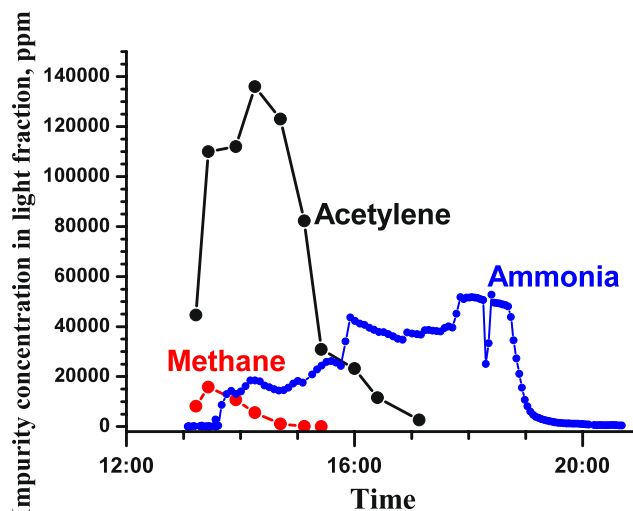
Fig. 7 Monitoring of impurities in light fraction of PH$_3$ from sampling time (time at which sample is removed)

in the samples of the light fractions by the TDLS method, together with Fourier spectrometer and gas chromatograph methods. In the samples of the light fraction of arsine, besides NH$_3$ such impurities as acetylene, phosphine and hydrocarbons were detected, and in the samples of the light fraction of phosphine, methane and acetylene were detected. Figure 7 shows a change in the impurity content in the light fraction sample of phosphine according to the data from the Fourier spectrometer and gas chromatography from the sampling time (the time in the process at which samples were extracted). It is evident that at first methane was taken away, then acetylene, and only after a rather long time (6 hours) ammonia was taken off.

In the process of the removing the arsine light fraction a separation process was also observed. At first more volatile phosphine was detected, then acetylene and then ammonia. Thus, it was found that ammonia is one of the basic impurities in arsine and phosphine, synthesized by hydrolysis of As$_2$Mg$_3$ and P$_2$Mg$_3$ in the solution of hydrochloric acid.

4 Conclusion

With the aid of the TDLS method the continuous monitoring of the NH$_3$ content in the sampling of the light fraction, middle cube and lower part of the distillation column in the

process of AsH$_3$ and PH$_3$ low-temperature purification was successfully realized and tested.

It was found that, in the solutions of arsine and phosphine, NH$_3$ manifests the properties of more volatile impurity with respect to these hydrides, although judging by their boiling points, NH$_3$ must be less volatile. During the purification of arsine and phosphine, ammonia is taken off longer than all highly volatile impurities. Therefore the continuous monitoring of the NH$_3$ content in the light fraction is necessary in order to determine the moment of the end of ammonia removal.

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