CHARACTERIZATION OF HIGH PURITY ARSINE AND GALLIUM ARSENIDE EPILAYERS GROWN BY MOCVD

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Introduction: The purity of the arsine process gas used for MOCVD can significantly influence the performance of high-speed transistors and high-brightness optoelectronic devices. Even trace levels of dopants, such as Ge, O or S incorporated into GaAs, InAlAs and AlGaAs structures from impurities in the arsine gas will generate energy levels in the forbidden energy gap, that change the electrical and optical properties of the host semiconductor. In this presentation, arsine samples purified with different methods and characterized using gas analysis techniques were used to grow GaAs epilayers. Since oxygen incorporation is particularly important to device performance, purifier studies were performed to investigate the capability of removing water vapor from the arsine. In addition, an arsine cylinder depletion study was performed to test the consistency of gas purity as the cylinder contents were consumed. Since gas analysis is limited by the detection sensitivity of instrumentation, low temperature photoluminescence of the GaAs epilayers has been performed to evaluate the arsine gas purity.

1. Arsine Gas Characterization Studies

1.1 Removal of Key Impurities Many impurities in crude arsine such as hydrogen sulfide, carbon dioxide and water vapor can be removed using chemical and adsorption purification. However, impurities such as GeH_4, PH_3 and hydrocarbons are more difficult-to-remove to very low levels. Distillation is very effective for purifying the arsine Data in FIG. 1 shows that all impurities were removed to below the lower detection limit (LDL) of instrumentation. For example GeH_4, a critical impurity for III-V devices, was reduced from 4.4 ppbv down to <30 pptv levels after the distillation, measured by GC-ICP-MS.

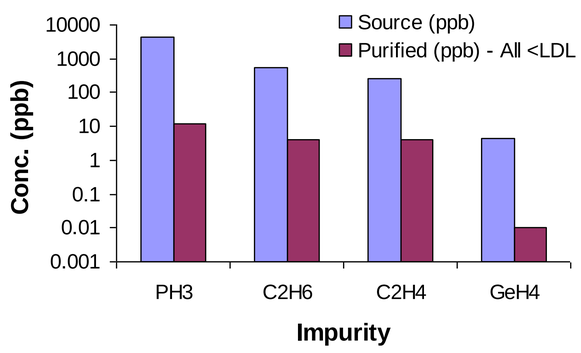

FIG.1: Impurity removal by distillation from arsine

1.2 H_2O Impurity Removal Oxygen incorporation in V/III device is particularly detrimental to device performance and water vapor is the primary source for oxygen impurity. So, water vapor removal from arsine gas is very important for semiconductor processes. FIG. 2 shows the removal of water vapor in arsine gas from 580 ppbv to single ppbv within 2 hours, using a Nanochem ASX-II purifier. This measurement was performed using a CRDS.

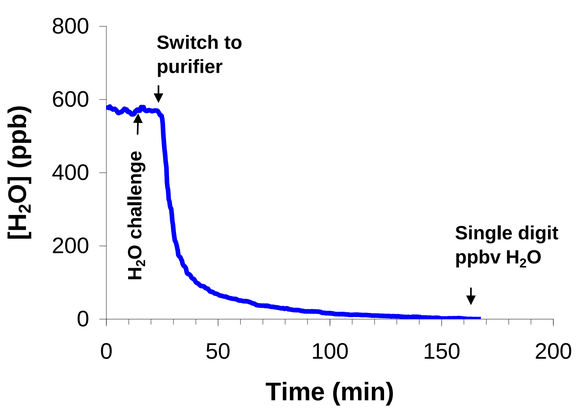

FIG.2: Time plot showing the reduction of water vapor in arsine, when a Nanochem ASX-II purifier (Matheson Tri-Gas, Longmont CO) is switched into the gas line.

1.3 Cylinder Depletion Study for H_2O H_2O is polarized molecule and will partition between the liquid and vapor phase AsH_3. As cylinder arsine is used in III-V device fabrication, it is important to know the moisture profile while the cylinder arsine is consumed. FIG. 3 shows that the H_2O in the arsine delivered from a high purity arsine cylinder remained at <10 ppbv until well after phase-break (7-8 lbs) and then increased only to 108 ppbv as the cylinder completely depressurized.

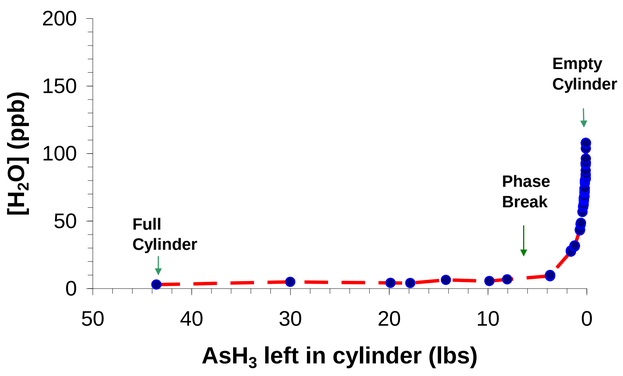

FIG. 3: H_2O impurity profiles in an arsine cylinder while the arsine is consumed.

Other impurities such as N_2, SiH_4 and CH_4, are non-polarized molecules and typically decrease as the arsine is consumed. For example, at the beginning, the cylinder had 50 ppbv N_2 and at 8 lbs remaining, 18 ppbv N_2 was measured in the arsine.

2. Arsine Performance Studies by GaAs PL

2.1 Experiment Details: In this experiment, three purified arsine samples with and without distillation were used for the GaAs PL study. The impurities in each cylinder are listed in Table 1.

Table 1 Impurity levels in three arsine cylinders for GaAs MOVPE

AsH_3 Sample	1	2	3
Purification	Distilled	Undistilled	Undistilled
Impurity	Conc. (ppbv)	Conc. (ppbv)	Conc. (ppbv)
N_2	36	17	25
O_2/Ar	<9	<9	<14
CO	<5	<5	<5
CO_2	<9.5	<9.5	<9.5
C_1-C_2 HC	<4	10	24
PH_3	<11.5	NA	NA
H_2S	<40	<40	<40
GeH_4	0.017	<3	<3
SiH_4	<3	<5	<5
H_2O	<50	<50	200

GaAs epitaxial layers (~ 10 µm) were grown by MOCVD at 650ºC using AsH_3 and TMG (V/III: 150) at flow rates of 176 and 8.8 sccm respectively. GaAs low temperature (10K) photoluminescence was excited by a He-Ne laser operated at 633 nm with an excitation power 0.0006 to 6 W cm^2.

2.2 High-purity GaAs Photoluminescence Figure 4 shows the PL spectrum of high-purity of GaAs (sample 1). Well resolved free and bound exciton emission in the range 1.512-1.516 eV shows typical n-type GaAs. The radiative decay of neutral acceptor bound exciton (A^0, X), neutral donor bound exciton (D^0, X), and the neutral donor bond vacancy (free holes) (h, D^0) are well resolved at 1.52123 eV, 1.5145 eV and 1.5134 eV. The upper and lower polariton branches of free exciton are clearly shown, which indicated a high-purity GaAs epilayer.

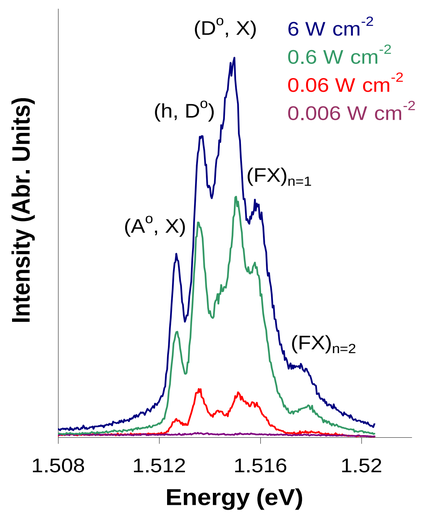

FIG. 4: Typical near band emission of high-purity n-type GaAs grown with arsine sample 1 at different pump levels.

2.3 C, Zn, Mg and Ge Impurities FIG. 5 shows the comparison of GaAs PL data for arsine samples 1 and 2. Compared with that of Sample 1, the FWHM of PL of Sample 2 decreased by 0.873 eV. In addition, (*D0*, *X*) intensity decreased greatly, (h, *D*) increased greatly, the lower level polariton branch disappeared and the upper level polariton branch decreased with extrinsic broadening (FIG. 5a).

Carbon is an intrinsic impurity incorporated from TMG. In addition to C impurity (e, C^o) at 1.4931 eV, Mg (e, Mg^0), Zn (e, Zn^0) and Ge (e, Ge^0) impurities were found in Sample 2 at 1.4917 eV, 1.489 eV and 1.479 eV (FIG. 5b). The Zn and Mg are likely to have come from TMG and contributed to the change in optical properties.

As shown in Table 1, the germane impurity in arsine sample 1 was 17 pptv and at this low level was not detected in the PL. We know that GeH_4 impurity in sample 2 was below 3 ppbv which may be the reason that it was detectable in Sample 2. However, it is still unclear what GeH_4 concentration in the arsine causes detectable Ge in the PL data.

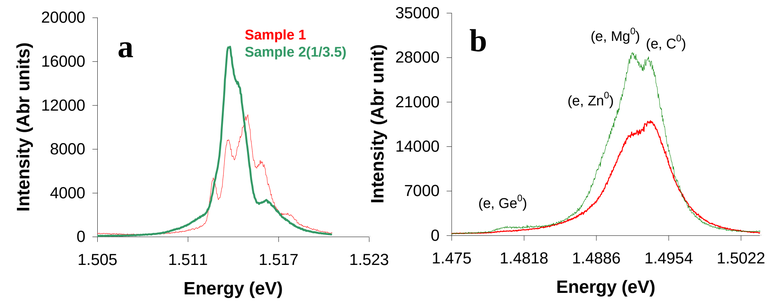

FIG. 5: Comparison of GaAs PL data for arsine samples 1 and 2: (a) Decrease of emission band width (FWHM), emission intensity of (D^0, X) and (F X), and increase of the emission intensity of (h, D^0) in near band emission spectrum; (b) Detection of C, Mg, Zn and Ge impurities in acceptor spectrum.

2.4 Water Vapor Impurity Oxygen impurity may be incorporated into GaAs from water in the arsine gas, resulting in high resistivity and semi-insulation. Generally, oxygen in GaAs has been identified as an As interstitial (O_i) and as an As antisite (O_{As}). The former is electrically inactive and the latter is electrically active. There is some controversy as to whether each or both are potential traps for quasi-free electrons and their affect on the free carrier concentration. The third aspect is the formation of an oxygen-donor (O-*D*) complex in GaAs, which may further complicate the influence of oxygen on the optical properties of GaAs.

Arsine Sample 3 had 200 ppbv H_2O, which may be responsible for the difference in near band emission of GaAs, including the decrease of the intensity of (D^0, X) and (F X), and the band emission FWHM, resulting in an overall quenching of PL (FIG. 6). The intensity of the (e, C^0) in sample 3 is much lower relative to that in sample 1. O-C complex formation could be a reason for this as such a complex might decrease the concentration of neutral carbon as an acceptor. However, it is not clear how this O-C complex influences the near band emission of GaAs.

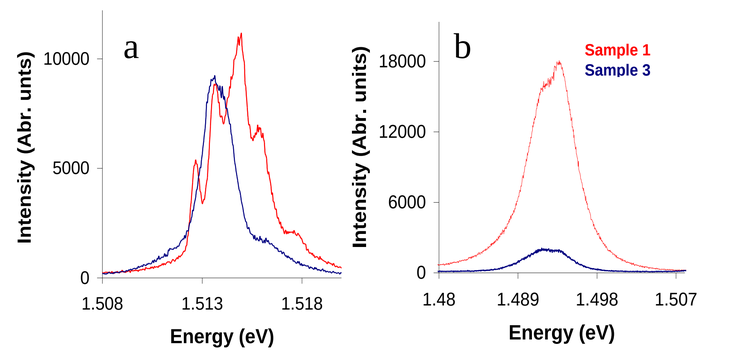

FIG. 6: Comparison of GaAs PL data for arsine samples 1 and 3 showing the affect of oxygen impurity on (a) the near band emission and (b) the acceptor spectra.

3. Conclusions

Gas analysis data and well-resolved exciton spectra of GaAs demonstrates the effectiveness of purification methods for manufacturing high-purity arsine. H_2O removal with ASX-II purifier to single digit ppb levels as well as the cylinder depletion data confirm consistent gas purity with use. The effect of oxygen on GaAs photoluminescence has been presented. However, further study is needed to understand how the oxygen changes the PL of n-type GaAs epilayers.

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