技術報告

ハードマスクプロセスアモルファスカーボン成膜用アセチレンガス精製装置 PICO-TRAP™の開発

Acetylene Process Gas Purification by PICO-TRAP™ Ashable Hard Mask for Amorphous Carbon Films

JHA Praveen*　DAVIA Dan*　SEYMOUR Adam*　TORRES Robert*
VININSKI Joe*

アセチレンガスはアモルファスカーボン成膜用に使用されている。アセチレンガスはその不安定な性質から，容器内では溶剤（アセトン）を含浸させた多孔質材に溶解させて保管されている。アセチレンガスを使用する際にはアセトン蒸気も同伴され，そのアセトン濃度は容器内残存量が減少するに連れて増加する傾向があり，残量がほぼ空に近い状態においては10% もの濃度に達する。このアセトン濃度の上昇はアモルファスカーボンの成膜速度が変化し，屈折率に悪影響を与える。

本報ではアセトン除去用ピコトラップの開発において，社内（アルファテスト）及びフィールド（ベータテスト）で得られた知見を報告する。本装置は物理，化学的にアセトンを除去するために系内の温度，圧力を最適化し，装置出口においては安定した低濃度のアセトンを含む精製アセチレンガスが得られる。本装置を導入することで，現状は最小1.34 MPa までのみ使用可能であったアセチレンガスが0.27 MPa の低圧力範囲まで使用可能となった。アセトン濃度はFT-IR を用いて定量し，また、成膜に悪影響を与える金属やパーティクル成分についても他分析機器を用いて，精製装置から排出されないことを確認した。

Acetylene gas is used for deposition of amorphous carbon films on wafers for etch processes. Because acetylene is unstable under pressure, it is stored in cylinders containing a porous substance saturated with solvent (acetone) to render it safe to store and use. As acetylene is discharged from these cylinders for use, acetone vapors are present in the gas phase. The concentration of acetone increases as gas phase acetylene is progressively withdrawn from the cylinder. Concentrations of acetone can approach 10%(v/v) in acetylene close to the point where the cylinder is fully depleted. The presence of acetone and its increasing concentration leads to inconsistencies in the rate of deposition of amorphous carbon films, leading to refractive index changes.

In this work, results from alpha and beta development of the PICO-TRAP™ AHM are presented. The PICO-TRAP™ AHM was developed to reduce the concentration of acetone in acetylene and provide a low, stable concentration of acetone throughout the depletion of the cylinder contents. This is accomplished by operating at optimal temperature and pressure to physically and chemically remove acetone in a continuous operation in order to maintain constant concentration in the acetylene exiting the purification system. This allows the consumption of a full cylinder (typically 1.82 MPa (250 psig)) down to 0.27 MPa (25 psig) without degradation of performance. Without purification, cylinders can be used typically only to 1.34 MPa (180 psig). The acetone concentration in acetylene was quantified using FT-IR spectroscopy. Additional analyses were performed via metals, gas chromatography and particle counting to ensure no added impurities were contributed from the PICO-TRAP™ AHM.

*Advanced Technology Center, Matheson Tri-gas Inc.

1. Introduction

In many applications for purified process gases there is an increased need for higher levels of purity. This need is acutely felt in the semiconductor fabrication industry, where increasing control and precision in the processing environment require gases that are exceptionally pure. However, the demand for higher purity gases has to be balanced with the cost and reliability of the systems used to supply those gases.

Sub-32 nm device design rules require high aspect ratio patterning for both logic and memory devices. At these advanced geometries the introduction of amorphous carbon films has enabled cost effective, high density patterning. Amorphous carbon films require precursors like acetylene. Acetylene purity and amorphous carbon film consistency is critical to device performance. Acetylene is filled in cylinders containing a porous substance saturated with solvent, such as acetone (dimethylformamide may also be used). The solvent in conjunction with the porous substance increases the capacity of the storage cylinders and helps stabilize the gas. However, when the acetylene is discharged from the cylinders, vapors of the solvent are present in the acetylene gas. The solvent vapors are the largest component of impurities in acetylene gas. Moreover, as the acetylene is being discharged from the storage cylinder, its concentration in the cylinder drops relative to the concentration of the solvent. This results in an increasing concentration of the solvent impurities in the acetylene over the lifetime of the cylinder. The full cylinder pressure of acetylene is about 1.82 MPa(250 psig) at room temperature conditions and the initial acetone concentration is about 0.25% -0.40 %. At later stages of cylinder depletion, the acetone concentration in acetylene can be 5% or more at cylinder pressures of less than 0.27 MPa(25 psig)[1, 2]. The increasing acetone concentration in acetylene leads to reduction in deposition rate of amorphous carbon films. Due to the changing concentration of solvent impurity in the acetylene, cylinder usage is limited to the period when solvent concentration is low and constant in the gas. This results in frequent cylinder change outs and wasted, unused gas. Without purification, acetylene cylinders typically can be used only to 1.34 MPa (180 psig).

In certain cases, the acetylene gas can be purified by adsorption to remove solvent impurities before being used in an application[3]. However, delivering purified acetylene with consistently low solvent impurities is challenging because the amount of impurities that needs to be removed is significant, and variable over time. The purifier needs to be able to accommodate changing impurity levels in the acetylene in order to produce a purified gas with a constant low level of the impurities.

At high flow rates of acetylene (15 L/min) and increasing acetone concentration, typical purifier materials may saturate or be consumed in a short amount of time. Typical purifier materials may also not be able to achieve low and constant acetone concentration. PICO-TRAP™ AHM purifies acetylene to levels of solvent impurities that are both low and constant, providing consistent rate of deposition of amorphous carbon films. Also it enables the use of more gas per cylinder, thereby, reducing the process costs by decreasing the amount of wasted gas and reducing the frequency of cylinder change-outs.

2. Experimental

2.1 Acetone removal experiments

PICO-TRAP™ AHM acetone removal tests were performed at Novellus Systems, Portland OR. The PICO-TRAP™ AHM performance was evaluated by recording acetone removal efficiency from acetylene. The acetylene source was connected to the PICO-TRAP™ AHM system as shown in **Fig. 1**. The flow rate of the gas was controlled by a mass flow controller (MFC) connected downstream of the PICO-TRAP™ AHM. The gas was diluted by nitrogen before entering the FT-IR for analysis. The acetone concentration was determined using the peaks in the region 2890-3050 cm^{-1}. The moisture concentration was determined using the peaks in the region 3570-3760 cm^{-1}. Standard spectral data for acetone provided by FT-IR manufacturer (MKS Instruments) was used for quantification. The acetylene cylinder pressure was monitored by an electronic gauge.

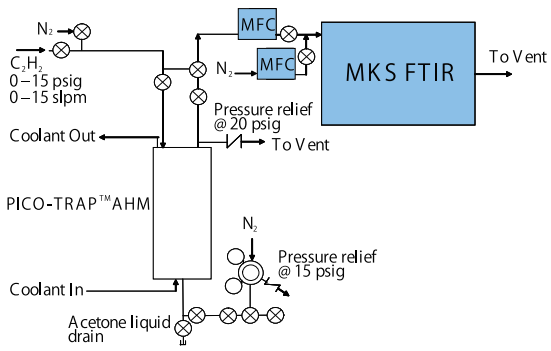

Fig. 1 Experimental setup for determining acetone removal efficiency of PICO-TRAP™ AHM.

2.2 Gas Sampling and Metals Analysis

Experiments were performed on PICO-TRAP™ AHM to determine if any metals, gas phase components, or particulates were added by the system during acetone removal from acetylene. The experimental setup to conduct these experiments is shown in **Fig. 2**.

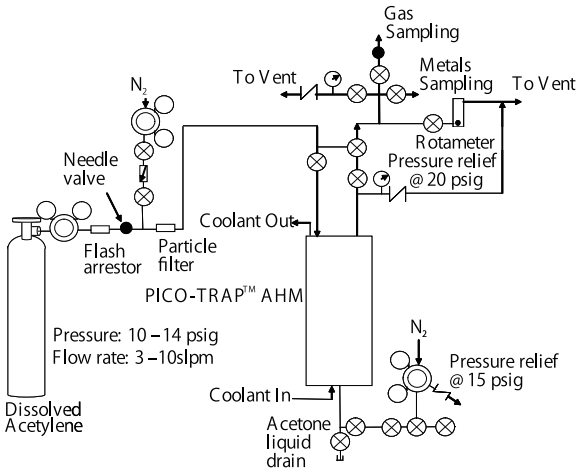

Fig. 2 Experimental setup for gas sampling and metals analysis for PICO-TRAP™ AHM.

Metals emission from the PICO-TRAP™ AHM and bypass were determined by hydrolysis sampling methods and ICPMS analysis according to best practices as defined in SEMI Specifications C30-1101, and C3.52-0200. Sampling was conducted by flowing acetylene gas from the cylinder to the Teflon capture vessel containing deionized/purified water; and bubbling the acetylene through the water for 46 minutes. The experiment was repeated using the same experimental apparatus and same experimental conditions (flow rate, temperature and pressure), but the acetylene gas was directed through the operating PICO-TRAP™ AHM so that a direct comparison of the two data sets could be obtained. The operating temperature of the PICO-TRAP™ AHM was -45℃ . The hydrolysis samples were then analyzed via High Resolution Inductively Coupled Plasma / Mass Spectrometry (ICP/MS). The results from the ICP/MS analysis are reported as the concentration of the impurities in the acetylene gas in ppb w/w, with typical detection limits in the low ppb range that is dependent on each specific metal.

Analysis of Hydrocarbon and Sulfur Impurities

Analysis of volatile hydrocarbon impurities was conducted by collecting samples of the gas flowing through the bypass and through the PICO-TRAP™ AHM. The samples were analyzed by a calibrated gas chromatograph with thermal conductivity and flame ionization detection (TCD, FID). Chromatography conditions and columns were selected to achieve baseline separation of the impurities. Results are reported in ppm v/v, with a detection limit of 0.5 ppm.

Analysis of volatile sulfur impurities was conducted by collecting samples of the gas flowing through the bypass and through the PICO-TRAP™ AHM. The samples were analyzed by a calibrated gas chromatograph with sulfur chemiluminescence detection and the chromatography conditions and columns were selected to achieve baseline separation of the impurities. Results are reported in ppm v/v with a detection limit of 0.01 ppm.

Analysis of other hydrocarbon impurities was conducted by collecting samples of the gas flowing through the bypass and the PICO-TRAP™ AHM. Samples were analyzed by a calibrated gas chromatograph/mass spectrometer. Conditions, columns, and mass filters were selected to achieve good resolution and identification of the hydrocarbon species. Results are reported in ppm v/v with detection limit of 0.1 ppm.

Particles Analysis

A Particle Measuring Systems Inc., HPGP-101 laser particle counter was used to monitor particle concentrations in acetylene at a pressure of 0.17 MPa(10 psig). The pressure was selected to simulate the process conditions used in actual device manufacturing. The construction of the wetted gas lines was electropolished 316L stainless steel with VCR fittings. A mass flow controller in the sample outlet stream provides the necessary 0.003 m^3/min (0.1 cfm) that is directed into the particle counter. Use of the mass flow controller controls the flow to ±2%, independent for the range of 0.17 to 1.13 MPa (10 to 150 psig).

The particle counter has the ability to count 8 different sized particles simultaneously in the range from 0.1 to 5 microns. A baseline particle count of the sampling apparatus and lines was collected for a minimum of 25 minutes (0.07 m^3 (2.5 ft^3) of gas sampled). If zero particles were measured for this time period, particle counting of the test subject would then commence. The bypass and the PICO-TRAP™ AHM were measured for particles in one minute increments for a total of 25 minutes (0.07 m^3 (2.5 ft^3) of gas sampled). All particles measured by the particle counter were totaled and the final particle counts of the bypass and the PICO-TRAP™ AHM were reported.

3. Results and Discussion

3.1 PICO-TRAP™ AHM Alpha studies

This section provides the results from the alpha studies performed on PICO-TRAP™ AHM, where the acetone removal from acetylene performance was determined at various pressure and temperature conditions of the system.

The system as shown in Fig.1 was purged overnight with nitrogen through the PICO-TRAP™ AHM bypass. The FT-IR background was obtained in nitrogen through the PICO-TRAP™ AHM bypass. **Fig. 3** shows acetone removal efficiencies of the PICO-TRAP™ AHM obtained at various temperatures.

The acetylene flow was initially directed through the PICO-TRAP™ AHM bypass into the FT-IR. The acetone concentration in acetylene via the bypass was observed to be 0.61% at the cylinder pressure of ~1 MPa (130 psig). Acetylene flow rate was 8 slpm and the delivery pressure was 0.19 MPa (12.5 psig). After the initial bypass run, the acetylene was flowed into the PICO-TRAP™ AHM at room temperature and then the trap temperature was reduced. Stable acetone concentrations in acetylene exiting the PICO-TRAP™ AHM at various temperature conditions were observed and are shown in Fig. 3. The temperature of the PICO-TRAP ™ AHM was reduced to -20, -30, -35, -40 and -45 ℃ . The acetone concentrations at various temperatures are listed in **Table 1** for this experiment. The acetone concentration observed at -45 ℃ and 0.19 MPa (12.5 psig) operating pressure was 0.052%.

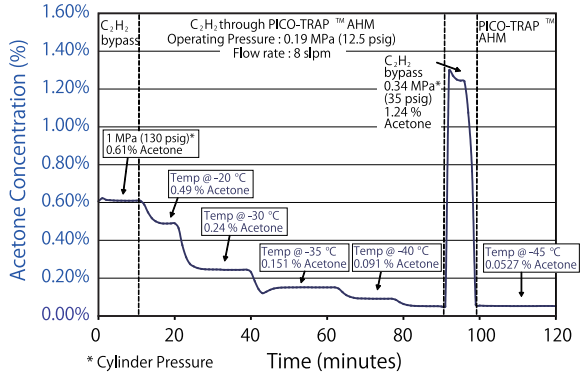

Fig. 3 Acetone removal efficiencies of PICO-TRAP™ AHM at various temperatures and constant pressure (12.5 psig)

After observing stable acetone concentration in acetylene at -45 ℃ , the PICO-TRAP™ AHM was bypassed and the acetylene cylinder was drained to 0.34 MPa (35 psig) cylinder pressure. After reaching the cylinder pressure of 0.34 MPa (35 psig), the acetone concentration in acetylene from cylinder was observed to be 1.24%. The gas was then flowed through the PICO-TRAP™ AHM which was operating at -45 ℃ and the acetone concentration in the acetylene stream exiting the PICO-TRAP™ AHM was observed to be 0.052%. This result showed that the acetone removal efficiency is independent of the challenge concentration.

Table 1 Acetone concentration in acetylene purified by PICO-TRAP™ AHM at various temperatures

Temperature (℃)	Acetone Concentration
Room Temperature	0.610%
-20	0.490%
-30	0.240%
-35	0.151%
-40	0.091%
-45	0.052%

Operating Pressure variation study

Under the operating conditions of -45 ℃ and 0.19 MPa (12.5 psig) for PICO-TRAP™ AHM, the acetone concentration in the purified acetylene was stable at 0.052%. The operating pressure was varied between (0.16 to 0.19 MPa) 9.2 to 13.1 psig at -45 ℃ . The acetone concentrations in acetylene exiting the PICO-TRAP™ AHM at various pressures are shown in **Fig. 4**.

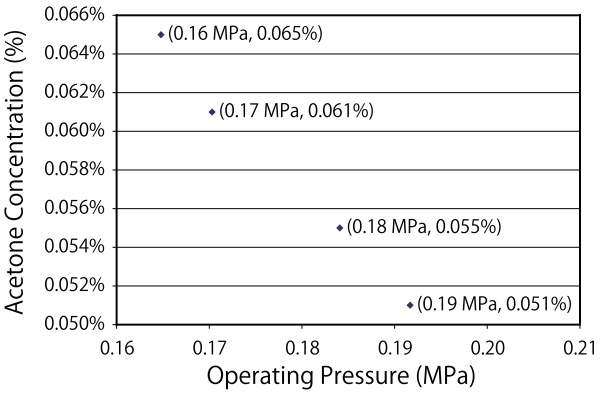

Fig. 4 Acetone removal efficiencies of PICO-TRAP™ AHM with varying pressures at -45 ℃ .

Transient study

The PICO-TRAP™ AHM exit valve was closed and opened a few times and the acetone concentration response was recorded. There were no spikes in acetone concentration observed during this experiment as shown in **Fig. 5**.

Ambient temperature variation study

The PICO-TRAP™ AHM was covered with a plastic sheet to observe the change in acetone concentration due to a change in ambient temperature. The heat exhaust from the chiller warmed the outside of the PICO-TRAP™ AHM. The ambient temperature variation did not produce any change on the acetone removal efficiency as shown in **Fig. 5**.

Acetone concentration long term stability

The acetylene flow through PICO-TRAP™ AHM at −45 ℃ was run overnight with a delivery pressure of 0.19 MPa (12.5 psig). At the start of the experiment, the acetone concentration in acetylene (bypass PICO-TRAP™ AHM) was recorded to be 0.73% and the cylinder pressure was 1.13 MPa (150 psig). The results from this experiment are shown in **Fig. 6**. PICO-TRAP™ AHM consistently removed acetone from acetylene for more than 14 hours. The concentration of acetone in acetylene exiting the PICO-TRAP™ AHM was 0.052%+0.002% over the entire experiment.

Due to the presence of moisture in acetylene there is a possibility of ice or acetylene hydrate formation in the PICO-TRAP™ AHM during operation. The constant acetone concentration indicates that there was no formation of ice or acetylene hydrate in the PICO-TRAP™ AHM during the course of the experiment. At the end of the experiment, the acetone concentration in acetylene (bypass PICO-TRAP™ AHM) was 1.00% (compared to 0.73% at the outset of the 14 hour experiment) at a cylinder pressure of 0.47 MPa (53 psig) (compared to 1.13 MPa (150 psig)).

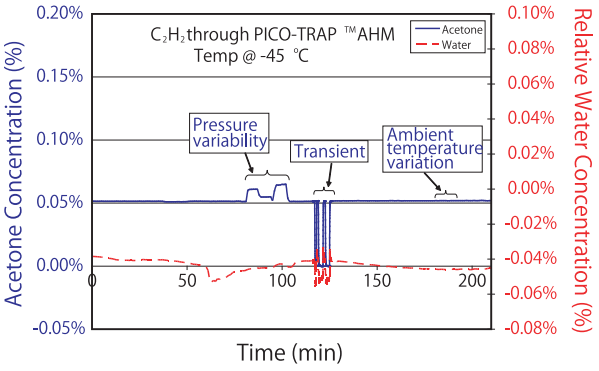

Fig. 5 PICO-TRAP™ AHM performance with pressure variation, transient operation and ambient temperature variation.

Fig. 6 also shows relative moisture concentration in the acetylene. The moisture concentration in acetylene through PICO-TRAP™ AHM was lowered to a consistent level from a higher moisture concentration in the cylinder.

3.2 PICO-TRAP™ AHM Beta studies

The alpha studies as described earlier provided two important conclusions. First, the acetone concentration in acetylene was reduced and remained constant through PICO-TRAP™ AHM purification independent of acetylene flow and acetone challenge concentration. The acetylene flow was varied in

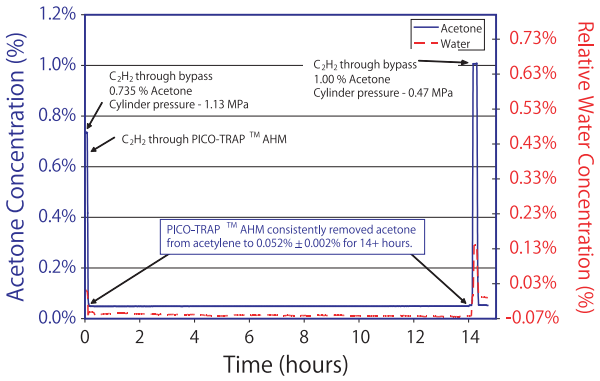

Fig. 6 Acetone concentration long term stability of PICO-TRAP™ AHM.

the range 3–15 slpm. The acetone concentration in acetylene exiting the PICO-TRAP™ AHM was 0.052% at operating temperature of −45 ℃ and 0.19 MPa (12.5 psig) pressure. Second, the PICO-TRAP™ AHM performed consistently over long period of time which indicated that there was no ice or acetylene hydrate formation.

In the alpha studies, liquid acetone collected in the PICO-TRAP™ AHM was not removed continuously. This liquid acetone collected had to be removed manually through a valve for the drain and further purged with nitrogen. The Beta design included a drain system that removed liquid acetone continuously from the PICO-TRAP™ AHM.

The liquid acetone is formed in the PICO-TRAP™ AHM during the process of purifying acetylene and this liquid acetone is removed continuously from the system without any interruption of the process acetylene flow. This drain system consists of an orifice through which acetone liquid is removed from the PICO-TRAP™ AHM system. At the downstream side of the orifice there is vacuum applied by a venturi. This vacuum venturi is operated by high pressure N_2 which also dilutes the liquid acetone to the point that it vaporizes. The exhaust of N_2 and acetone vapor is appropriately scrubbed.

Fig. 7 shows the performance of PICO-TRAP™ AHM at an operating temperature of −45 ℃ with varying acetylene cylinder pressures. As shown in the figure, the challenge acetone concentration increases from 0.40% at 1.76 MPa(240 psig) to 1.40% at 0.27 MPa(25 psig) while the PICO-TRAP™ AHM maintains the acetone concentration at 0.052%+0.002% in acetylene exiting the system. The acetylene flow through the PICO-TRAP™ AHM was varied in the range of 5–15 slpm during these experiments and the operating pressure varied in the range of 0.18–0.19 MPa (12–13 psig). The desired

target spec for acetone concentration in purified acetylene is 0.052%+0.015%. PICO-TRAP™ AHM performance was much better than the desired target spec in both alpha and beta studies.

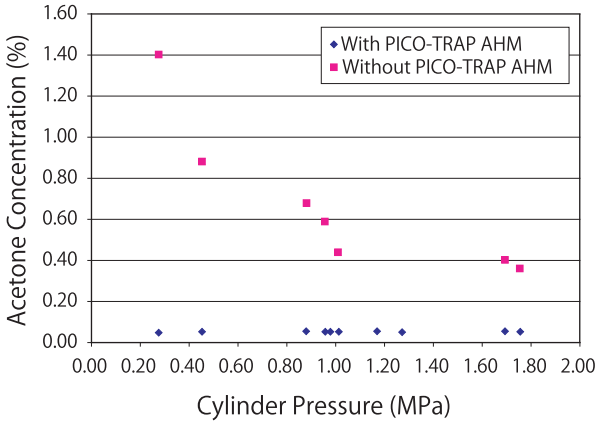

Fig. 7 PICO-TRAP™ AHM performance for acetone removal with varying acetone challenge concentration.

3.3 Gas Sampling and Metals Analysis

Further investigation focused on the removal of additional impurities present in the acetylene gas and verification that the PICO-TRAP™ AHM does not emit any impurities. A full set of analytical tests was conducted for a completely full cylinder (1.82 MPa, 250 psig) and again after > 90% of the cylinder was consumed. For the second set of analytical measurements the pressure in the cylinder was less than 0.27 MPa(25 psig). All the analyses discussed in this section were performed at the PICO-TRAP™ AHM operating temperature of −45 ℃ . For direct comparison, samples were obtained by flowing acetylene through the same sampling manifold, with the PICO-TRAP™ AHM either on-line or in bypass.

Table 2 shows results from metals analysis of PICO-TRAP™ AHM and bypass at the two cylinder pressures. The investigation included hydrolysis sampling with high resolution ICP/MS analysis to identify and quantify 40 volatile and non-volatile metals. PICO-TRAP™ AHM outperformed the bypass for metals.

Volatile hydrocarbon analysis was conducted for methane, propane, isobutene, n-butane, 1-butene, isopentane, n-pentane, and hexane via Gas Chromatography with TCD and FID detectors enabling the determination of concentrations down to less than 1 ppm levels. **Table 3** shows the results from hydrocarbon analysis. Methane was observed to be the major impurity in the acetylene from cylinder. Methane is volatile and is partitioned in the head space of the acetylene cylinder, as high values were observed for high cylinder pressure. PICO-TRAP™ AHM did not remove methane from acetylene.

Table 2 Metals data in acetylene from full and depleted cylinders via PICO-TRAP™ AHM and Bypass

Full Cylinder at 1.83 MPa(250 psig)				Depleted Cylinder at < 0.27 MPa(25 psig)			
Element	Bypass (ppb)	PICO-TRAP (ppb)	Detection Limit (ppb)	Element	Bypass (ppb)	PICO-TRAP (ppb)	Detection Limit (ppb)
Li	ND	ND	1.5	Li	ND	ND	1.5
Be	ND	ND	0.6	Be	ND	ND	0.6
B	ND	ND	3.0	B	ND	ND	3.0
Mg	2.1	ND	1.5	Mg	1.8	ND	1.5
Al	7.1	ND	1.5	Al	ND	ND	1.5
Ti	ND	ND	3.0	Ti	ND	ND	3.0
V	ND	ND	0.6	V	ND	ND	0.6
Cr	ND	ND	1.5	Cr	ND	ND	1.5
Mn	ND	ND	1.5	Mn	ND	ND	1.5
Ni	ND	ND	3.0	Ni	ND	ND	3.0
Co	ND	ND	1.5	Co	ND	ND	1.5
Cu	ND	ND	1.5	Cu	ND	ND	1.5
Ba	ND	ND	0.6	Ba	ND	ND	0.6
Zn	1.8	ND	1.5	Zn	1.8	ND	1.5
Ga	ND	ND	0.6	Ga	ND	ND	0.6
Ge	ND	ND	1.5	Ge	ND	ND	1.5
As	ND	ND	3.0	As	ND	ND	3.0
Sr	ND	ND	0.6	Sr	ND	ND	0.6
Zr	ND	ND	0.6	Zr	ND	ND	0.6
Nb	ND	ND	0.6	Nb	ND	ND	0.6
Mo	ND	ND	1.5	Mo	ND	ND	1.5
Ag	ND	ND	1.5	Ag	ND	ND	1.5
Cd	ND	ND	1.5	Cd	ND	ND	1.5
Sn	ND	ND	1.5	Sn	ND	ND	1.5
Sb	ND	ND	0.6	Sb	ND	ND	0.6
Si	ND	ND	8.9	Si	ND	ND	8.9
Ta	ND	ND	0.6	Ta	ND	ND	0.6
W	ND	ND	1.5	W	ND	ND	1.5
Au	ND	ND	1.5	Au	ND	ND	1.5
Tl	ND	ND	0.6	Tl	ND	ND	0.6
Pb	ND	ND	0.6	Pb	ND	ND	0.6
Bi	ND	ND	0.6	Bi	ND	ND	0.6
Th	ND	ND	1.5	Th	ND	ND	1.5
U	ND	ND	1.5	U	ND	ND	1.5
Fe	ND	ND	1.5	Fe	ND	ND	1.5
Na	2.4	ND	1.5	Na	17.5	ND	1.5
Ca	47.3	1.7	1.5	Ca	26.8	ND	1.5
K	2.4	ND	1.5	K	5.1	ND	1.5
P	ND	ND	5.9	P	ND	ND	5.9
S	ND	ND	5.9	S	7.1	ND	5.9
Total Metals Measured Above Detection Limit	63.1 ppb	1.7 ppb		Total Metals Measured Above Detection Limit	60.1 ppb	ND	

Table 3: Volatile hydrocarbons in acetylene from full and depleted cylinders via PICO-TRAP™ AHM and Bypass

Full Cylinder at 1.83 MPa(250 psig)			Depleted Cylinder at < 0.27 MPa(25 psig)		
Impurity	Bypass (ppm)	PICO-TRAP (ppm)	Impurity	Bypass (ppm)	PICO-TRAP (ppm)
Methane	73	60	Methane	0.5	0
Propane	0	0	Propane	0	0
Propylene	0	0	Propylene	0	0
Isobutane	0	0	Isobutane	0	0
n-Butane	0	0	n-Butane	0	2.2
1-Butene	0	0	1-Butene	0	0
Other Butenes	0	0	Other Butenes	0	0
Isopentane	0	0	Isopentane	0	0
n-Pentane	0	0	n-Pentane	0	0
Hexanes	0	0	Hexanes	0	0

Detection limit of analysis was 0.5 ppm

Table 4 shows the results from volatile sulfur species analysis that was conducted using gas chromatography with sulfur chemiluminescence detection. Hydrogen sulfide was observed to be present in acetylene. Similar levels of hydrogen sulfide were found in acetylene flow through PICO-TRAP™ AHM and bypass.

Table 4 Volatile sulfur species in acetylene from full and depleted cylinders via PICO-TRAP™ AHM and Bypass.

Full Cylinder at 1.83 MPa(250 psig)			Depleted Cylinder at < 0.27 MPa(25 psig)		
Impurity	Bypass (ppm)	PICO-TRAP (ppm)	Impurity	Bypass (ppm)	PICO-TRAP (ppm)
Hydrogen Sulfide (H_2S)	0.04	0.06	Hydrogen Sulfide (H_2S)	0.04	0.02
Sulfur Dioxide (SO_2)	0	0	Sulfur Dioxide (SO_2)	0	0
Carbonyl Sulfide (COS)	0	0	Carbonyl Sulfide (COS)	0	0
Methyl Mercaptan	0	0	Methyl Mercaptan	0	0
Ethyl Mercaptan	0	0	Ethyl Mercaptan	0	0
Dimethyl Sulfide	0	0	Dimethyl Sulfide	0	0
Carbon Disulfide	0	0	Carbon Disulfide	0	0
t-Butyl Mercaptan	0	0	t-Butyl Mercaptan	0	0
Isopropyl Mercaptan	0	0	Isopropyl Mercaptan	0	0
n-Propyl Mercaptan	0	0	n-Propyl Mercaptan	0	0
Methyl Ethyl Sulfide	0	0	Methyl Ethyl Sulfide	0	0
2-Butyl Mercaptan	0	0	2-Butyl Mercaptan	0	0
i-Butyl Mercaptan	0	0	i-Butyl Mercaptan	0	0
Diethyl Sulfide	0	0	Diethyl Sulfide	0	0
n-Butyl Mercaptan	0	0	n-Butyl Mercaptan	0	0
Dimethyl Dsulfide	0	0	Dimethyl Dsulfide	0	0
Unknown Volatile Sulfur	0	0	Unknown Volatile Sulfur	0	0

Detection limit of analysis was 0.01 ppm

Other impurities such as methanol, 1-buten-3-yne, 1,3-butadiyne, trans-1,2 dichloroethylene and benzene were observed in acetylene. The removal of these impurities to a certain extent was observed using PICO-TRAP™ AHM as shown in **Table 5**. The detection limit for analysis of these impurities was 100 ppb.

Table 5 Concentration of other hydrocarbon impurities detected in acetylene from full and depleted cylinders via PICO-TRAP™ AHM and Bypass

Full Cylinder at 1.83 MPa(250 psig)			Depleted Cylinder at < 0.27 MPa(25 psig)		
Impurity	Bypass (ppm)	PICO-TRAP (ppm)	Impurity	Bypass (ppm)	PICO-TRAP (ppm)
Methanol	18	4	Methanol	44	5.5
1-Buten-3-yne	3	2.7	1-Buten-3-yne	12	4.6
1,3-Butadiyne	2	0.1	1,3-Butadiyne	7.2	0
Trans-1,2 Dichloroethylene	36	0.1	Trans-1,2 Dichloroethylene	32	4.1
Benzene	3.6	0.9	Benzene	0.8	0

Detection limit of analysis was 0.1 ppm

Table 6 (a) and (b) show the results from particle counting analysis. The analysis was performed in purified nitrogen and acetylene. Gases were flowed through a stainless steel particle filter of size 0.003 µm for both bypass and PICO-TRAP™ AHM particle counting experiments as shown in Fig. 2. Similar results were obtained for particle counts through PICO-TRAP™ AHM and bypass.

Table 6 Particle analysis data in nitrogen and acetylene via PICO-TRAP™ AHM and Bypass.

(a) Particle Counts in Nitrogen

	Bypass	PICO-TRAP
Pressure(psig)	10	10
Volume(cu. ft.)	2.5	2.5
Total Particles	2	1
Particles per cu. ft.	0.8	0.4

(b) Particle Counts in Acetylene

Full Cylinder

	Bypass	PICO-TRAP
Pressure(psig)	10	10
Volume(cu. ft.)	2.5	2.5
Total Particles	2	1
Particles per cu. ft.	0.8	0.4

Empty Cylinder

	Bypass	PICO-TRAP
Pressure(psig)	10	10
Volume(cu. ft.)	2.5	2.5
Total Particles	2	1
Particles per cu. ft.	0.8	0.4

In each case, the results of the various analyses showed that the bypass impurity concentration was greater than or equal to the PICO-TRAP™ AHM. The PICO-TRAP™ AHM was not adding impurities into the acetylene gas phase stream.

In addition, the empirical data demonstrated that the

concentrations of the impurities for the bypass were higher than the concentrations observed from the gas that was flowed through the PICO-TRAP™ AHM for metals, hydrocarbons, various sulfur containing species, methanol, and higher molecular weight hydrocarbons.

4. Conclusion

Dissolved acetylene when discharged from a cylinder contains considerable amounts of solvent (acetone) impurity. The solvent concentration increases as the acetylene gas is progressively withdrawn from the cylinder.

PICO-TRAP™ AHM is useful in removing and maintaining the acetone concentration in acetylene at a constant low level. Analytical tests conducted with FT-IR instruments and field tests conducted in collaboration with Integrated Device Manufacturers (IDM's) have demonstrated that the use of the PICO-TRAP™ AHM effectively reduces and holds constant the presence of acetone in acetylene. This results in a higher and more stable deposition rate for amorphous carbon films.

PICO-TRAP™ AHM consistently removes the acetone from acetylene down to 0.052%+0.002% at operating conditions of −45 ℃ and 0.19 MPa (12.5 psig) independent of the acetone challenge concentration and acetylene flow rate in the range of 5 – 15 slpm. This result outperforms the acetone concentration specification of 0.052%+0.015% desired by the IDM's for stable deposition rate of amorphous carbon film. Moreover, the liquid acetone formed in the PICO-TRAP™ AHM during acetylene purification is removed by a continuous drain system.

The PICO-TRAP™ AHM acetone removal performance was also tested by variation in pressures, transient flow disruption, and ambient temperature changes. The long term acetone stability data showed that there was no ice or acetylene hydrate formation in the system. Further studies by gas sampling, metals analysis and particle counting validated that the PICO-TRAP™ AHM was not emitting or adding impurities into the acetylene gas phase stream. PICO-TRAP™ AHM has demonstrated that acetylene cylinders can be used down to 0.27 MPa (25 psig). This allows for more use of the product within the cylinder and minimizes cylinder change-outs that can be a productivity, safety, and contamination concern.

References

1. Ness, C., "The Safe and Efficient Handling of Dissolved Acetylene" , Union Carbide Corporation 1958, p.43-48.
2. Yasuo, K. et. al., (US Patent 4863493), "High Purity Acetylene Gas" , September 5 1989.
3. Miller, S. A., "Acetylene – Its Properties, Manufacture and Uses" , Vol 1, British Oxygen Company 1965, Academic Press- New York and London, p.330-363.