

## 高純度 HBr 容器に関するオージェ電子分光メトリーを用いた 金属酸化表面の調査と水分発生メカニズムに関する研究

### Auger Electron Spectrometry Investigation of Metal Oxide Surfaces and Mechanism for Moisture Generation in Ultra-High Purity HBr Cylinder Packages

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半導体エッチングプロセスに用いられる無水 HBr は厳しい不純物コントロールが要求される。HBr を使用するプロセスにおいて、容器材質は不純物のコントロールや高純度を達成する上で重要な因子となるため、注意深く選択しなければならない。本研究では、AISI 4130 Cr-Mo 合金に Ni ライニングを施した容器と一般産業で標準品として用いられる AISI 4130 Cr-Mo 合金について (a) HBr に暴露した後のシリンダー内表面粗 / 表面積の比較、酸化膜層形成の厚さ、(b) HBr をガス相で供給した際の水分濃度の比較を行った。一年以上経過した後、研磨された標準品の Cr-Mo 容器の表面粗さは Ni ライニングのシリンダーと比較して2倍であった。また、Cr-Mo 容器における酸化層の侵食は Ni ライニングと比較して10倍以上であった。そして最後に、Ni ライニングの表面は AISI 4130 Cr-Mo 合金の表面より不活性であり、HBr ガス中の水分濃度は Ni ライニングなしの AISI 4130 Cr-Mo 合金の場合に比べ4倍程度低かった。これら2つの容器について水分発生メカニズムを比較検討した結果、AISI 4130 Cr-Mo 合金に Ni ライニングを施した容器は超高純度 HBr を保存、供給するために適した材料であることが明らかとなった。

Anhydrous HBr used in etch processing for the semiconductor industry requires strict impurity control. However, the gas cylinder material of construction plays a critical role in controlling and maintaining purity levels of the delivered HBr process gas and must be carefully selected. In this work Ni-lined AISI 4130 Cr-Mo steel cylinders are compared against the gas industry standard AISI 4130 Cr-Mo steel cylinders with regard to (a) surface roughness/area and oxide layer thickness after exposure to HBr and (b) the concentration of moisture in delivered HBr gas. Over the period of a year, the surface roughness increase of the polished Cr-Mo steel package doubles that of the Ni-lined package and the penetration of the oxide layer into the metal for the Cr-Mo steel is over 10 times that for the Ni surface. Finally the more inert surface of the Ni lining is shown to lower the moisture concentration in the HBr gas by ~4 times. The mechanism for moisture generation from the two packages will be considered and will be offered as speculation on the reason for higher moisture levels in Cr-Mo steel cylinders compared to Ni-lined cylinders. These findings demonstrate that Ni-lined AISI 4130 Cr-Mo steel provides a superior package for Ultra High Purity HBr storage and delivery.

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## 1. Introduction

Minimizing impurities in corrosive etch gases, such as HBr, is crucial for reaching and surpassing the 65nm node in advanced semiconductor device processing. Research and testing of various alloys and materials for corrosive gas delivery systems has optimized impurity reduction<sup>1,2)</sup>. Corrosion resistance and moisture control has been the primary focus of the design and alloy choice for delivery systems. Alloys such as Nickel 200 and Hastelloy C-22 have demonstrated high performance in HBr when compared to AISI 4130 Cr-Mo steel and alloy 316L stainless steel<sup>3,4)</sup>. However, these materials are significantly expensive and not practical for cylinder package applications.

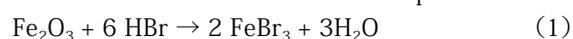
Applying corrosion control technology to the cylinder package significantly reduces the impurities delivered in HBr. Historically, the standard cylinder material used in the semiconductor industry for HBr is AISI 4130 Cr-Mo steel. However, Ultra High Purity (UHP) applications require more stringent impurity control, and therefore demand the use of alternate cylinder materials. Conventional alloy applications such as Hastelloy® C-22 and Nickel 200 are not cost effective when applied to cylinder sized packages for HBr, due to the significant amount of material required and the lack of availability from the cylinder manufacturers. Thus, UHP HBr applications must employ stainless steel or electroless Ni plating. These alternate alloys can strongly influence molecular impurities found in the gas, such as gas phase moisture and corrosion products such as metal bromide particles.

Elevated moisture in HBr leads to corrosion of the delivery components, which generates molecular and particulate impurities, thereby increasing the probability of contamination on the wafer. Vapor phase moisture in HBr also inhibits wafer chemistries and ultimately increases the likelihood of defects on the chip. As the features on the wafer decrease in size, an increased emphasis on optimized moisture control in HBr is needed. Requirements for UHP HBr specify <1ppm gas phase moisture concentration. In order to meet these requirements, Ni-lined AISI 4130 Cr-Mo steel cylinders provide a more inert surface, which reduces water generation in HBr, as compared to polished 4130 Cr-Mo steel.

The first phase of this study was performed to establish whether Ni-lined cylinders provide a new

cost-effective level of moisture control beyond the AISI 4130 Cr-Mo steel package.

The second phase of this study focused on the metal oxide layers on the interior surface of the HBr cylinder that depend on the surface material and moisture level of the gas. It is predicted that the surface of AISI 4130 Cr-Mo steel cylinders develop thick iron bromide layers when exposed to HBr over time. The oxide layers on the interior of the cylinder are expected to react with HBr producing molecular and particulate by-products that entrain in the vapor phase of the delivered gas. The reaction shown below provides the mechanism for the in-situ formation of moisture when iron oxide is exposed to HBr.



The Enthalpy of formation for this reaction (1) is unknown, but the equivalent reaction with HCl and  $\text{Fe}_2\text{O}_3$  is -145 kJ/mol, indicating the HCl reaction is thermodynamically favorable. The analogous reaction in HBr is also expected to be thermodynamically favorable and the reaction is expected to proceed. In addition to water produced by the reaction of the oxides with the HBr, it is expected that the inherently porous and thick native oxide layer present on the Cr-Mo steel surface is a large contributor to the formation of excessive amounts of water after HBr is first introduced into the cylinder. Alternatively, the dense and very thin oxide layer present on the nickel surface minimizes the amount of moisture generated in the nickel lined cylinders.

In addition to the moisture that is generated due to the reaction of the metal oxide with the HBr, it is expected that chemisorbed water is also present on the surface of the metal oxide and is removed when the hygroscopic HBr material removes the attached water from the surface. This effect has been observed for several process gases such as ammonia, arsine, and HCl. Empirical evidence for this effect is shown in **Fig. 1** below. The results indicate the after the particle filter is completely dried down in nitrogen, a burst of moisture is observed from both metal and Teflon filters when an ultra-dry process gas is introduced. These results demonstrate that strongly bound, chemisorbed moisture cannot be removed by inert gas purging, but can be removed when hygroscopic molecules are introduced to the surface. The hygroscopic materials tend to interact strongly with the chemisorbed moisture and remove the moisture from the surface and insert the water into the gas stream.

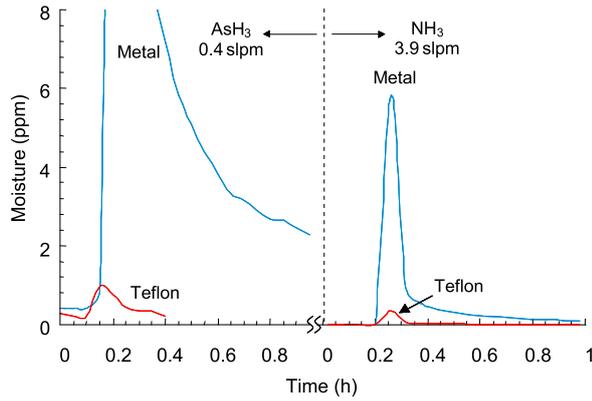


Fig. 1 Chemisorbed water emission from Teflon and metal particle filters in ultra dry process gas, after being dried down to less than 100 ppb in  $N_2$ .

The final phase of the experiment created a theoretical model that predicts the total surface area of the cylinder based on average empirical surface roughness measurements. The overall surface area helps estimate the total surface oxide availability to react with the packaged gas. It is predicted that high surface area will have high impurity levels in the stored gas.

## 2. Experimental

### 2.1 Phase 1 – Surface Oxide Analysis

A total of four cylinder samples were selected for depth profiling of the surface. Two samples were AISI 4130 Cr-Mo steel cylinders that had been in UHP HBr service for >1 year. One sample was collected from a Ni-lined AISI 4130 Cr-Mo steel cylinder that had been in UHP HBr service for >1 year. The last sample was a new, polished AISI 4130 Cr-Mo steel cylinder that was used as a control sample.

The sample cylinders were drained of the HBr via gas phase release. The cylinders were then cycle purged from 0.54MPa(gauge) to atmospheric pressure for >80 cycles with purified nitrogen to eliminate residual HBr remaining in the cylinder. Once properly drained and cycle purged, the samples were cut into sample coupons using a high purity, lubricant-free cutting system, to eliminate the addition of hydrocarbons or other contaminants to the sample surface during the cutting process. All samples were analyzed by Auger Electron Spectroscopy (AES) depth profiling within six hours of cutting, in order to eliminate variations from atmospheric oxidation.

Surface oxide measurements were performed by AES, which is capable of detecting Auger electrons

from near surface atoms in all elements except H and He. The method is capable of detecting 0.1-1 atomic % with a depth resolution of 20-200 Å during depth profiling mode. The lateral resolution measurement on the profile is 5-10  $\mu\text{m}$ . The depth profiling is performed by using AES while simultaneously sputtering target with a 2.0 keV  $\text{Ar}^+$  beam. The samples were sputter depth profiled to a depth of 1000 Å.

### 2.2 Phase 2 – Surface Profilometry and Visual Inspection

Immediately following the cutting of the cylinders for coupons the cylinders were visually inspected, photographed, and measured for surface roughness.

The surface roughness measurements were obtained using a portable surface profilometer (MahrFederal Providence, RI). The profilometer utilizes a piezoelectric probe to measure surface heights over a lateral automated probe drag. The absolute measurements of the surface are then converted to a mean surface roughness  $R_a$  (DIN EN ISO 4287, ASME B46.1).

$$R_a = (1/L) \int_0^L |Z(x)| dx \quad (2)$$

Where  $Z(x)$  = profile ordinates of the depth profile<sup>6)</sup>. Three independent sites on the cylinder surface were measured at the top, middle, and bottom sections of each cylinder, a total of nine measurements were taken from each cylinder. The measurements were then averaged for the mean cylinder roughness.

Using the average cylinder roughness calculated from the nine independent sites in the cylinder, the total cylinder surface area was calculated using a surface area model. The surface model uses the assumption that all peaks are the same height and trough as well as peak to peak distance. The model also assumes that each surface peak pyramid in shape.

### 2.3 Phase 3 – Moisture Analysis

All experiments were performed in a well ventilated area in order to prevent exposure to HBr. Sampling lines and components were constructed of Hastelloy® C-22 to minimize corrosion and to avoid any impurity contribution from the system that is not from the test cylinder. The sample lines were heated to 65°C to prevent variation from adsorption/desorption of moisture on the sample manifold walls. For each experiment, 32 kg of UHP HBr liquid was filled in either a polished AISI 4130 Cr-Mo steel

cylinder or a Ni-lined AISI 4130 Cr-Mo steel cylinder. Prior to filling all of the cylinders were passivated and equilibrated using the same procedures. The gas was sampled at a rate of 0.7 standard liters per minute. The experimental conditions and procedures were established by a previous study determining the thermodynamic properties of trace moisture in HBr<sup>5)</sup>.

Gas phase moisture data was collected with a model MTO-1000 CRDS instrument (Tiger Optics, Warrington PA) using the absorption peak at 1392.54 cm<sup>-1</sup> which arises from the rotational transition (2,0,2 ← 3,0,3) in the  $\nu_1 + \nu_3$  (1,0,1 ← 0,0,0) vibrational band of water molecule. The calibration of the instrument was confirmed using a NIST certified H<sub>2</sub>O standard which was verified using a CR-3 chilled mirror hygrometer (Buck Research Instrument, Boulder CO) in nitrogen flow.

### 3. Results and Discussion

The results from the Auger Electron Spectrometry (AES) surface oxide analysis demonstrate that the polished AISI 4130 Cr-Mo steel exhibited much deeper oxide formation relative to the nickel lined cylinder. **Fig. 2** shows the oxygen level for the polished steel is dominant and constant for more than 1000 Å. In addition, the Br level is easily visible and constant to the same depth. The presence of oxygen to that depth is an indication that the porous oxide layer exists very deep into the bulk of the surface. It is possible that the oxide formed once the sample was re-exposed to the atmosphere, however, this result also indicates a porous film easily capable of gas and liquid penetration. The result that the Br level remains constant up to 1000 Å is also an indication that the reaction of HBr and metal oxide is taking place well into the bulk of the material and contributing moisture and corrosion products to the cylinder. Contrary to the steel results, the Ni lining significantly inhibits the oxide depth on the surface of the cylinder. **Fig. 3** shows the oxide depth profiles found in Ni-lined AISI 4130 Cr-Mo steel when exposed to HBr for greater than one year. The depth profile of the Ni-lined cylinder shows that the majority of the surface oxide penetrated less than 100 Å into the Ni surface, and is completely eliminated at a depth of 500 Å. Results were very similar with Br. The presence of Br was completely eliminated at a depth of approximately 500 Å. At this point in the depth of the sample, only the bulk

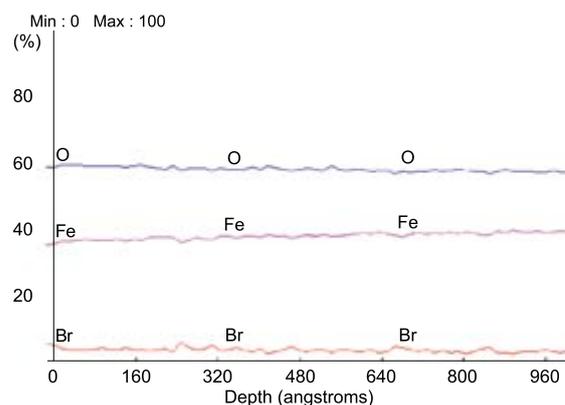


Fig. 2 AES sputter depth profile of a polished 4130 Cr-Mo steel cylinder after >1 year HBr exposure.

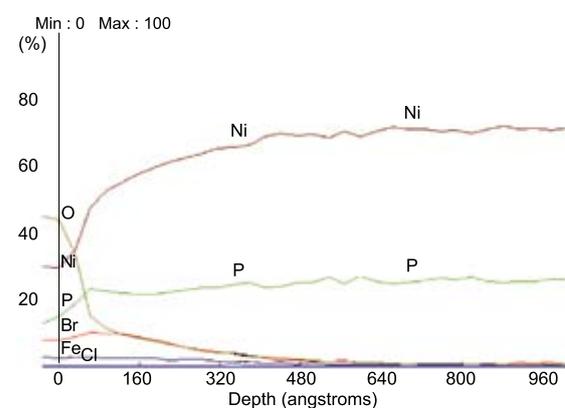


Fig. 3 AES sputter depth profile of a Ni lined 4130 Cr-Mo steel cylinder after >1 year HBr exposure.

constituents of the nickel lined remain and consist of nickel and phosphorus.

The lower oxide depth in Ni-lined cylinders reveals the relatively low reactivity of the Ni surface to the HBr. This lowered reactivity can lead to benefits such as lower moisture over the life of the cylinder, and a decreased likelihood of halogen salts being delivered in the gas phase.

The results from the surface profilometry support the inert characteristics of the Ni-lined surface vs. the polished Cr-Mo steel surface. Severe degradation of the cylinder surface roughness profile occurred during long term exposure in Cr-Mo steel cylinders. The average surface roughness in the polished AISI Cr-Mo steel cylinders increased by greater than 10 times when exposed to HBr for over one year, while the Ni-lined Cr-Mo steel cylinders had a roughness 5 times that of polished Cr-Mo steel.

Applying the surface roughness data to the surface area model effectively calculates the change in surface area of the cylinder surface. The break down

in surface roughness effectively adds approximately 6 times the surface area when compared to the original polished surface, while the Ni-lined cylinders only increased by a factor of 3.3 over the period of a year (Table 1). A lower surface area is expected to provide fewer surface interaction sites between the gas and cylinder surface. Additionally, lower surface reactivity leads to less impurity generation and reaction of the HBr over time, as demonstrated from the nickel lined cylinders. This phenomenon allows for a longer shelf life of the packaged HBr in the Ni-lined Cr-Mo steel cylinders vs. the traditional polished Cr-Mo steel cylinders.

The moisture studies conducted in Phase 3 of this study revealed that the Ni-lined AISI 4130 Cr-Mo steel cylinders outperformed the polished AISI 4130 Cr-Mo steel cylinders (Fig. 4). The Ni-lined cylinders consistently delivered moisture levels lower than 1 ppm. The average vapor phase moisture for all Ni-lined cylinders was 3.8 times lower than that of the polished Cr-Mo steel cylinders. The lower delivered vapor phase moisture is most likely a function of the less reactive and decreased quantity of surface oxides present in the Ni-lined cylinders.

Table 1 Surface profilometry and total cylinder surface area projected from profilometry measurements.

Cylinder Type (44L)	Average Surface Roughness (Ra)	Total Surface Area (cm <sup>2</sup> )
Polished Control Cr-Mo Steel Cylinder	0.17	11516
Cr-Mo Steel Cylinder >1 Year HBr Exposure	1.73	66581
Cr-Mo Steel Cylinder >1 Year HBr Exposure	1.76	67709
Ni Lined Cr-Mo Steel Cylinder >1 Year HBr Exposure	0.97	38154

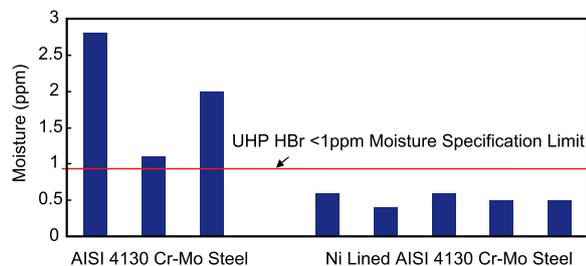


Fig. 4 Moisture comparison of AISI 4130 Cr-Mo steel and Ni lined AISI 4130 Cr-Mo steel HBr cylinders by CRDS.

#### 4. Conclusion

Cylinder package type has been demonstrated to have a large impact on the purity levels of ultra high purity hydrogen bromide. It has been established that the use of Ni alloys adds significant benefits to control contaminants that originate from the cylinder package. Results from all phases of the study revealed that interactions between the HBr and the cylinder package are minimized using a Ni-lined surface. The minimal interaction resulted in average HBr vapor phase moisture levels 3.8 times lower than average moisture from Cr-Mo steel cylinders. In addition to lower moisture, the surface degradation measured by AES demonstrated that the Ni-lined AISI 4130 Cr-Mo steel provided an inert surface that did not severely break down under long term anhydrous HBr exposure. The inert nature of the Ni-lined surface also led to a lower total surface area when compared to polished AISI 4130 Cr-Mo steel when exposed to anhydrous HBr for >1 year.

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