

Preparing a gas delivery system for excimer lasers with fluorine passivation of 316L stainless steel

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With the increasing demand in the semiconductor industry for critical line dimensions below 250 nm, microlithography has taken on greater importance, representing almost one-third of an IC's total production cost. The microlithography process, which produces

produce wavelengths of light between 248 and 157 nm. For example, exciting a blend of fluorine and krypton within a neon buffer produces light at 248 nm. Since microlithography is essential to semiconductor manufacturing and excimer lasers are crucial to microlithography, optimizing the use of fluorine and rare gases in excimer lasers is critical to the industry.

While the actual amount of fluorine fueling a laser is typically <0.2% by volume, it is usually delivered to the laser at con-

centrations between 1 and 5% and then diluted at the point of use by rare gases such as krypton or argon in neon. Although gas costs are a very small component of the overall microlithography cost of ownership (COO), their contribution can be magnified many times if gaseous impurities or insufficient fluorine are delivered to the laser.²⁻⁴ For

A study investigates the effects of fluorine on gas delivery systems used to supply excimer lasers and develops methods for passivating stainless steel with fluorine to reduce damaging impurities.

highly accurate microscopic, two-dimensional patterns in photosensitive resist material, relies on deep-ultraviolet (DUV) steppers and scanners to achieve linewidth reductions.¹ In turn, these new-generation tools derive their light from a type of gas laser known as excimer (short for *excited dimer*), which uses fluorine and rare-gas mixtures to

example, the “poisoning” of a laser with gaseous impurities can lead to days of downtime if the lasing chamber must be replaced. It is estimated that this worst-case scenario could cost a semiconductor manufacturer more than \$100,000 per

day per unit. Thus, to ensure maximum uptime performance, laser manufacturers must devote considerable attention to the quality of the lasing gas mixture. Qualified suppliers of photolithography-grade laser gas blends must demonstrate that their products and production processes adhere to OEMs’ strict performance and purity specifications.⁵

Ensuring gas quality at the point of use depends on the efficacy of the gas delivery system—an important link between the gas supply and the excimer laser. The impact of a poorly constructed and prepared delivery system can be devastating. For example, previous research has shown that when the inner surface of 304 stainless-steel tubing is first exposed to a gas blend containing 5% fluorine, tens of parts per million of hydrofluoric acid (HF), silicon tetrafluoride (SiF₄), carbonyl fluoride (COF₂), and carbon dioxide (CO₂) are produced by surface reactions.² These impurities, if they reach the laser during initial filling after hookup, can poison the laser cavity. Gas suppliers or laser manufacturers may be held accountable for such problems, even if they are not responsible for the construction and conditioning of the delivery manifold.

The increasing importance of fluorine and rare gases in the microlithography process has prompted end-users to investigate how best to store, handle, and deliver toxic gas mixtures. This article is part of that effort. It is based on a study conducted by Air Products and Chemicals (Allentown, PA) to develop passivation methods for preparing excimer-laser gas delivery systems and to understand the depth of fluorine penetration into 316L electropolished stainless steel, the material of choice for excimer-laser gas delivery systems, when exposed to 1–5% concentrations of fluorine.

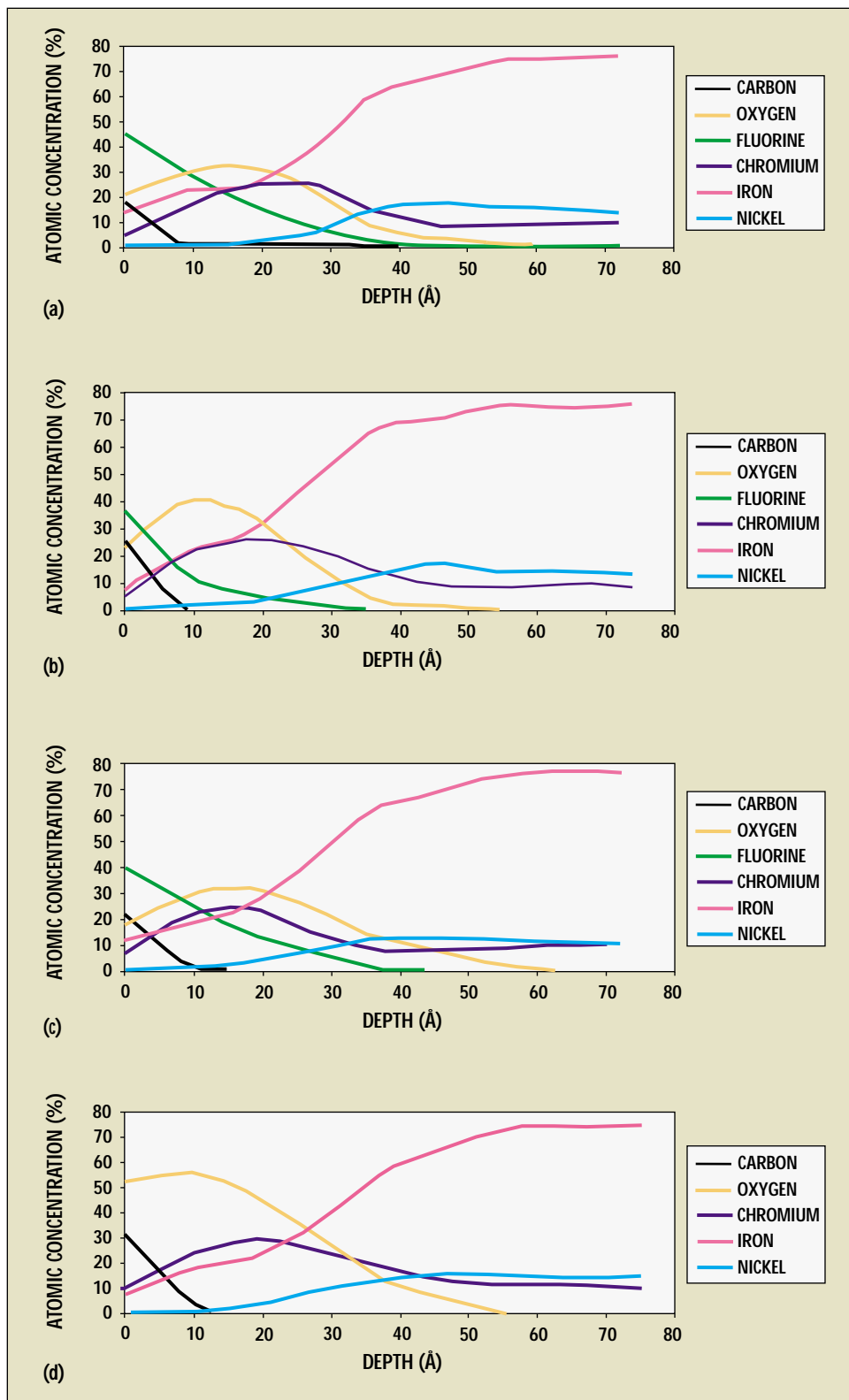


Figure 1: XPS depth profiles of 316L stainless-steel coupons exposed to (a) 1% fluorine for 92 days, (b) 1% fluorine for 72 hours, and (c) 5% fluorine for 24 hours. A depth profile for a blank (cleaned but untreated) coupon (d) is also shown for comparison.

Fluorine Passivation

Because fluorine is highly reactive, semiconductor manufacturers are particularly interested in knowing how to prepare or passivate a laser's gas delivery system before the introduction of process gases. Passivation is defined as the pretreatment of systems or components so that they will not react catastrophically with fluorine under normal operating conditions. The passivation process is commonly performed by exposing to gaseous fluorine all the surfaces of the system or components that are in contact with the gas under controlled conditions.⁶

A 1967 study reported that thin films (between 5 and 50 Å thick) rapidly form on structural metals but terminate on contact with fluorine-containing atmospheres. In a later study, those findings were validated using modern surface-analysis techniques.⁷ The later study also found that the penetration of fluorine into such materials as 302 stainless steel, copper, and brass was dependent on the fluorine concentration used. Subsequent research discovered that preexposing the inner metal surface to a 5% mixture of fluorine and nitrogen (or other inert gas) leads to the formation of a surface passivation film that minimizes sidewall reactions with tungsten hexafluoride.⁸

Recognizing the emerging need for high-purity laser gas delivery systems, another study reported on a pretreatment process using high concentrations of fluorine at elevated temperature to impart a very thick iron fluoride layer on the inner surface of pipes.⁹⁻¹¹ However, the cost and safety issues associated with performing a process using high temperatures and high concentrations of fluorine often make it very difficult to adopt within both new and existing semiconductor facilities that are tooling for DUV lithography.

Experimental Method

To investigate fluorine passivation and fluorine penetration into stainless steel, $\frac{3}{8} \times 1$ -in. coupons were cut from a 2-in.-diam 316L electropolished stainless-steel tube supplied by Valox (Ventura, CA). After cutting, the samples were cleaned by sonication in acetone for 3 minutes, air-dried, and sonicated again in methanol for another 3 minutes. After air-drying, they were stored in a dry nitrogen box until being exposed to fluorine. Just before the coupons were treated with fluorine, the cleaning procedure was repeated.

The coupons were exposed to blends of either 1 or 5% fluorine in neon in an experimental apparatus specifically designed for testing the compatibility of materials with reactive gases. Replicate coupons were exposed, at ambient temperature, to atmospheres containing either 1 or 5% fluorine at a pressure of 40 psig. To simulate the condition of the inner surface of an in-service pipe, two coupons were exposed for 92 days to a 1% fluorine-in-neon blend. This condition was selected because more than 99% of the current in-service excimer lasers for DUV lithography are charged with this blend. Additional 1%-fluorine exposures were performed for 24 and 72 hours. These times reflect current pas-

sivation practices in the field. In addition, treatments were also performed with 5% fluorine for 6 and 24 hours.

After an exposure was completed and the gas cell was purged with nitrogen, the coupons were unloaded within a nitrogen glove box and mounted onto a platen for analysis by x-ray photoelectron spectroscopy (XPS). The coupons were transferred within an inert vessel to the spectrometer just before analysis.

XPS analyses and ion-sputter depth profiling were performed on a 5000LS XPS system (Physical Electronics, Eden Prairie, MN). Sputter depth profiling was performed using an argon ion beam at a sputter rate of 36 Å/min as measured against a silicon dioxide standard. Quarter-minute intervals were employed to maximize data from the treatment zone. To minimize the recontamination of the surface between sputter intervals, the analysis time was minimized by using a pass energy of 58 eV. A high-resolution scan of the surface was performed at a pass energy of 23.5 eV before depth profiling commenced. Quantification was performed with the photoelectron cross sections embedded in the spectrophotometer's operating system. An untreated blank coupon was also prepared and analyzed for comparison.

Experimental Results

Figure 1 shows the depth profiles obtained for the coupons exposed to 1% fluorine for 92 days, 1% fluorine for 72 hours, and 5% fluorine for 24 hours. For reference, the depth profile of an untreated coupon is also presented. It was found that even after 92 days, the fluorine penetrated only to what is known as the near-surface region of the material. The fluorine primarily resided within the enriched chrome oxide layer that is always present on the surface of 316L electropolished stainless steel.

Surface compositional information collected before depth profiling is listed in Table I. After fluorine exposure, the surface of the 316L stainless steel had a higher concentration of iron, apparently at the expense of the chrome oxide passivation film. An abundance of fluorine was also present and, surprisingly, a decrease in the amount of surface carbon.

As seen in Figure 2, the F1s spectra for all of the treatments revealed great variations in how the surface fluorine was distributed between two chemical states: fluorine as metal fluoride (MF) and fluorine as organic fluoride (CF_x). The relative distribution of MF and CF_x was computed by curve fitting the F1s spectra for the two chemical states before depth profiling. The plot suggests that the chemical form of fluorine on the metal surface depends more on exposure time than on fluorine concentration. With increasing exposure time, a shift from CF_x to MF can be seen. This is caused by two factors:

1. Over time, the thin film of surface hydrocarbon slowly reacts with fluorine to form volatile CF_4 , thus "cleaning" the metal surface of this hydrocarbon contamination.
2. The fluorine primarily reacts with the iron present within the chrome oxide layer through a diffusion-controlled process.

Treatment	Carbon (% Atomic)	Oxygen (% Atomic)	Fluorine (% Atomic)	Chromium (% Atomic)	Iron (% Atomic)
Untreated 316L stainless-steel coupon	30.8	52.3	—	8.8	7.9
1% fluorine for 92 days	16.8	20.7	45.0	4.4	13.1
1% fluorine for 72 hours	25.7	22.5	38.5	5.3	8.0
1% fluorine for 24 hours	20.2	25.3	36.1	6.5	11.9
5% fluorine for 6 hours	27.7	22.2	38.4	4.0	7.7
5% fluorine for 24 hours	22.6	17.9	40.3	7.1	12.1

Table I: Results of XPS compositional analysis.

Reaction of Fluorine with Carbon. Validating the reaction between fluorine and carbon is experimentally difficult because the metal surface becomes recontaminated as soon as the coupons are removed from the reactor and transferred to the surface spectrometer. The adventitious hydrocarbon observed during the analyses of the posttreated coupons is thought to originate from this transfer process. Evidence to support this hypothesis is based on two observations.

First, considerably less adventitious carbon is measured on the surfaces of the treated coupons than on the blank. As shown in Table I, the surface of the blank coupon contained 30.8% carbon, while the fluorine-treated surfaces contained between 16 and 28% carbon. Because all of the coupons were identically cleaned before undergoing fluorine treatment, it was expected that the relative amounts of carbon present before use did not vary greatly across the sample set. But while clean metal-oxide surfaces are known to readily adsorb hydrocarbon contamination present in the atmosphere above them, the presence of fluorinated hydrocarbon raises the surface free energy, so that less hydrocarbon can be re-adsorbed after the metal is removed from the fluorine-containing atmosphere.

Second, the relative distribution of fluorinated carbon on

the surface undergoes a dramatic change over time. Figure 3 presents the relative distribution of fluorinated carbon on the surfaces of the treated coupons. These measurements were obtained by curve fitting the C1s spectra and measuring the peak area for each component. After 90 days, the distribution favored more CF₃ and CF₂ on the surface than CF. In addition, on an absolute carbon basis, the 90-day treated surface contained significantly less fluorinated carbon. These findings tend to support the conclusion that surface hydrocarbon reacts over time with the fluorine to produce CF₄, which is volatile.

These findings illustrate the need to properly clean a piping system before the introduction of fluorine. If the inner surface possesses a very thick film of hydrocarbon, the reaction between fluorine and the surface can produce appreciable levels of CF₄ within large runs of pipe over a long period of time. One study has shown that CF₄ at levels above 50 ppm can have a negative impact on the pulse energy of high-repetition-rate ArF excimer lasers, which are used for 193-nm lithography.³ CF₄ buildup may also inhibit the uptake of fluorine by the metal because of the presence of a blanketing layer of carbon. As the metal begins to finally take up fluorine long after being placed in service, surface reactions will re-

release impurities such as HF, CO₂, COF₂, and SiF₄. These species are known to have a severe effect on laser performance at the single parts-per-million level.²

To further understand the transition from surface CF_x to MF over time, the F1s spectra collected during depth profiling were fitted to separate the CF_x and MF contributions. Across all of the treatments, the CF_x contribution was quickly reduced to 0% within the first sputter interval, or 10 Å. Figure 4 shows the MF depth profiles for the treatment set. These profile plots reveal that

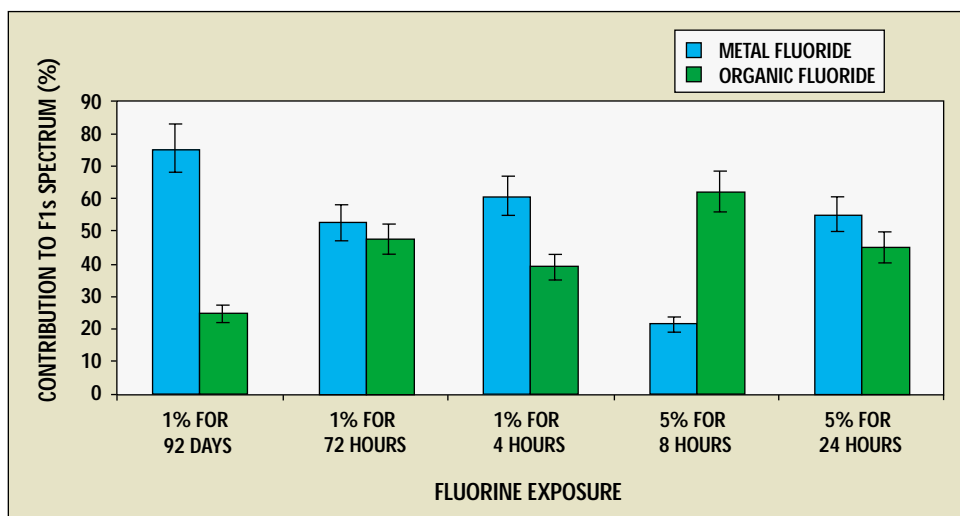


Figure 2: Curve fits of F1s spectra detailing the relative amounts of fluorine present as metal fluoride (MF) and organic fluoride (CF_x) on the metal surface before depth profiling for the various treatments.

the amount of fluorine incorporated within the treatment zone depends on both exposure time and fluorine concentration. Coupons treated with 5% fluorine for 24 hours had almost the same level of fluorine incorporated just below the very topmost atomic layers as the coupons treated with 1% fluorine for 92 days. Thus, although the carbon on the surface reacted with the fluorine, the fluorinated carbon film was sufficiently thin to allow fluorine to penetrate and react with the metal within the near-surface region. The time dependence of fluorine penetration and reaction is illustrated by the fact that fluorine uptake for a 5% treatment for 6 hours was similar to that for 1% treatments for 24 and 72 hours.

Gas costs are a small part of the microlithography COO, but their contribution can be magnified if gas impurities or insufficient fluorine are delivered to the laser.

Reaction of Fluorine with Iron. The metal fluorides within the near-surface region of the stainless steel were discerned by curve fitting the Cr2p and Fe2p XPS spectra. For the untreated coupon, the data indicate that chrome was present as Cr_2O_3 (576.6 eV) and iron primarily as FeO (709.7 eV). A very small peak at 706.6 eV was seen, indicating that some iron metal existed within the region of analysis, which was typically 15 to 20 Å deep. The iron metal was most likely present along the grain boundaries within the chrome oxide layer, just below the topmost atomic layers. The iron metal was present in the mean free path of the photoelectrons at between 15 and 20 Å.

After 92 days of treatment with 1% fluorine, a significant amount of Cr_2O_3 was still visible. At the same time, a new peak appeared

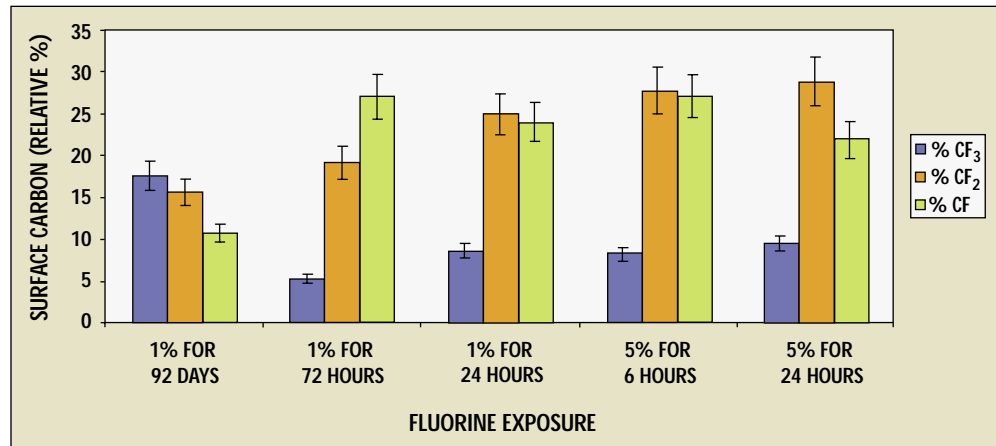


Figure 3: Curve fits of C1s spectra showing the relative distribution of fluorinated carbon present on the surfaces of the treated coupons.

at 578.4 eV that did not line up well with reference spectra for known chrome fluorides (CrF_3), leading to the hypothesis that it may have been caused by the presence of chrome oxyfluorides ($\text{Cr}_x\text{O}_y\text{F}_z$) that formed as the fluorine penetrated through the chrome oxide layer. Iron existed primarily as FeF_2 (710.9 eV), with a small amount of FeF_3 (714.2 eV). For all of the treatments, a distribution of these chrome and iron species could be observed.

An analysis of the depth profiles indicates that iron and chrome were perhaps being redistributed as a result of fluorine exposure. The ratio of chrome to iron had been used in the past to evaluate the suitability of 316L electropolished stainless steel for delivering ultra-high-purity gases.^{12,13} Figure 5 illustrates Cr/Fe depth profiles for the various treatments. Progressing from the untreated blank to the 1% fluorine treatment over 92 days, a definite enrichment of the original chrome oxide layer with iron occurred, which depended on both the length of exposure to and concentration of fluorine. The Cr/Fe profile for the 24-hour, 5% fluorine treatment closely approached that for the 92-day, 1% treatment.

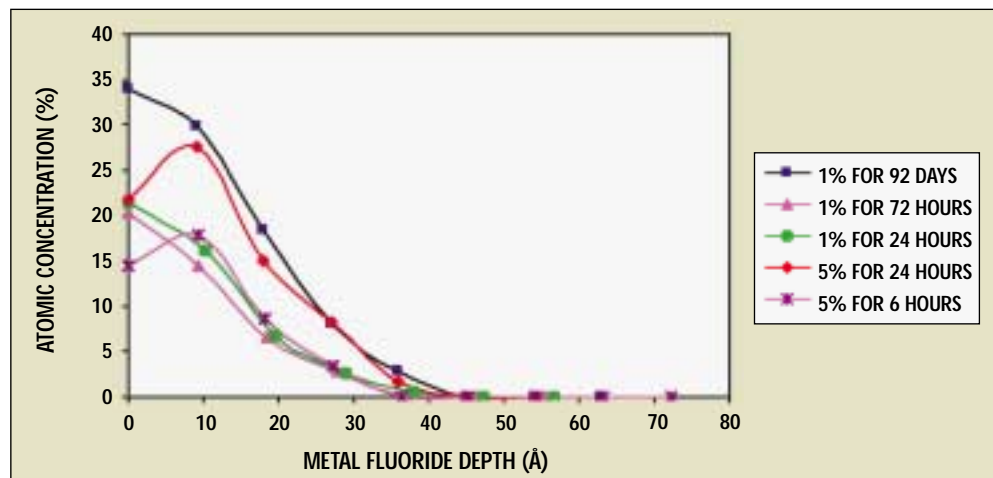


Figure 4: XPS depth profiles for the metal fluoride (MF) contribution to the F1s spectrum for the various fluorine treatments.

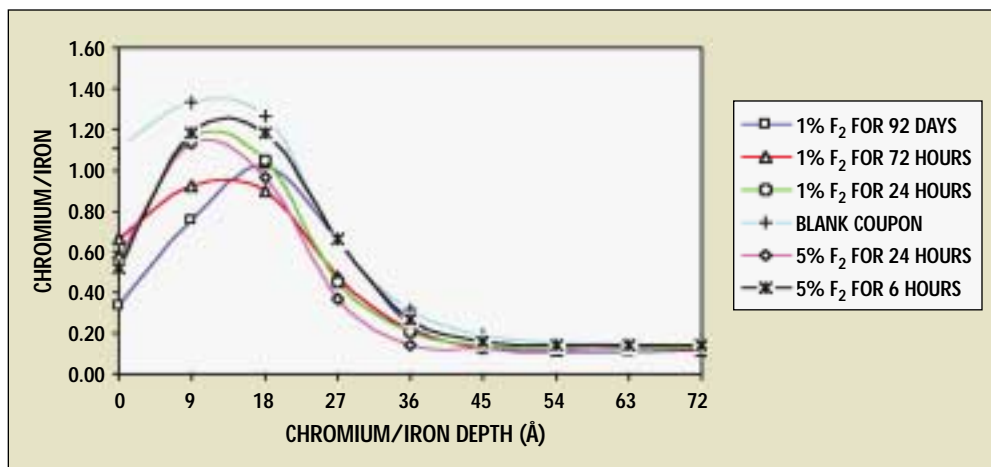


Figure 5: Chromium/iron depth profiles for various fluorine treatments. A blank (cleaned but untreated) coupon is presented for reference.

The enrichment of iron at the metal surface and the lack of fluorine depth penetration beyond the original chrome oxide layer suggest that the diffusion of iron from the bulk through the chrome oxide is a very important process in the overall uptake of fluorine by 316L electropolished stainless steel at room temperature. The data do not appear to support the conclusion that iron enrichment results from the loss of chromium through the formation of volatile chrome fluorides.

Figure 6 compares the chromium depth profiles for the blank coupon and for the coupons treated with 1% fluorine for 92 days in a different manner than usual. Because XPS-based concentration measurements are based on normalization to 100%, an attempt was made to absolutely quantify the amount of chromium present by examining the area counts computed under the Cr2p spectrum. Using this methodology, if a loss of chromium near the surface through volatilization occurs, a concomitant decrease in the emission of Cr2p photoelectrons should be measured. But the data indicate that there was very little, if any, change in the total

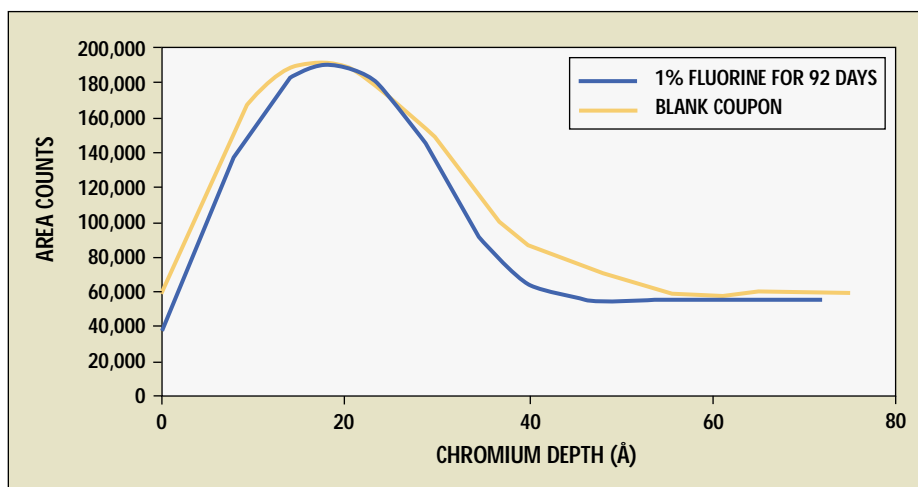


Figure 6: A comparison of the chromium (Cr2p) depth profile for coupon treated with 1% fluorine for 92 days and a blank (cleaned but untreated) coupon. Area counts are used to evaluate the absolute photoemission intensity for chromium within the analysis region.

amount of chromium in the near-surface region. Thus, the loss of chromium through the formation of volatile chrome fluorides was not a major contributor to the iron-enrichment process observed as a result of exposing 316L electropolished stainless steel to fluorine for prolonged periods of time at ambient temperature.

Conclusion

Fluorine treatment of 316L electropolished stainless steel at room temperature does not quickly lead to a thick, stoichiometric surface fluoride film.⁹⁻¹¹ Rather, the uptake of fluorine is slow, dependent on fluorine concentration, and limited to the topmost 50 Å of the metal. The process appears to occur as iron migrates from the bulk through the chrome oxide layer to the surface for reaction with fluorine. As a result, fluorine uptake is limited by the ability of iron to diffuse along the grain boundaries to the surface. By passivating the metal surface with a mixture of 5% fluorine and rare gases for 24 hours, fluorine uptake can be accelerated, thus slowing its further uptake in the future.

While hydrocarbon films on the surface of the material also fluorinate, they do so at a much slower rate than iron. It is postulated that they eventually convert to volatile CF₄ and enter the gas phase. While pipes that are properly cleaned before passivation emit only minimal amounts of CF₄ into the process gases, an unclean system may contain appreciable amounts of carbon that can contaminate the process gases and affect laser performance. Moreover, thick carbon films can impede the passivation of the metal surface during the initial conditioning period so that fluorine will eventually penetrate through the carbonaceous layer and into the near-surface area of the metal, resulting in the release of other, more harmful impurities.

When preparing a laser gas delivery system for excimer lasers, it is recommended that the piping system be thoroughly precleaned. It should then be passivated as soon as possible using a mixture of 5% fluorine in helium, neon, or argon for 24 hours. Fluorine blends with nitrogen are not suggested because of the negative impact nitrogen can have on laser performance. After the passivation mixture has been

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vented and purged, the line should be immediately charged with process gas.

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