



## ADVANCES IN THE UNDERSTANDING OF LOW MOLECULAR WEIGHT SILICON FORMATION AND IMPLICATIONS FOR CONTROL BY AMC FILTERS

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### Abstract

Trimethylsilanol (TMS) is a low molecular weight/low boiling point silicon-containing, airborne contaminant that has received increased interest over the past few years as an important cause for contamination of optical surfaces in lithography equipment.

TMS is not captured well by carbon-based filters, and hexamethyldisiloxane (HMDSO), even though captured well, can be converted to TMS when using acidic filter media commonly used for ammonia removal. TMS and HMDSO coexist in a chemical equilibrium, which is affected by the acidity and moisture of their environment.

This publication shows that HMDSO is converted to TMS by acidic media at concentrations typically found in cleanroom environments. This is contrary to published results that show a recombination of TMS to HMDSO on acid media.

We also demonstrate that, based on its conversion to TMS, HMDSO is not a suitable test compound for hybrid chemical filter performance, as the apparent lifetime/capacity of the filter can be substantially skewed toward larger numbers when conversion to TMS is involved. We show lifetime test results with toluene and HMDSO on acidic and non-acidic filter media.

Appropriately designed, asymmetric hybrid chemical filters significantly minimize or eliminate the conversion of HMDSO to TMS, thereby reducing the risk to scanner optical elements. Similarly, such filters can also prevent or reduce acid-sensitive reactions of other airborne molecular contamination (AMC) when passing through filter systems.

### Introduction

Silicon containing hydrocarbons are a class of AMC causing persistent degradation of UV exposure tool optical surfaces.<sup>1,2,3</sup> Organic silicon compounds are efficiently split into components by 193 nm UV light, commonly used in photolithography applications. The resulting, reactive silicon atoms can recombine with oxygen to create a layer of amorphous silicon dioxide on optical surfaces such as exposure tool lenses.<sup>3,4</sup> This haze layer can be difficult to remove and may require lens exchange and polishing, potentially destroying optical coatings and creating substantial tool downtime and cost. The importance of TMS and related refractory species in optical degradation is one reason for the low level of allowable refractory compounds (100 ppt) specified in the International Technology Roadmap for Semiconductors (ITRS) roadmap for lithography cleanroom ambient environments.<sup>5</sup>

The main source for TMS in fabs is the break-down path of hexamethyldisilazane (HMDS), used in photoresist coaters, which can subsequently leak into the cleanroom.<sup>6</sup> However, TMS can also infiltrate from ambient air, as it is emitted in substantial amounts from landfills<sup>7</sup> and it has been found to be a breakdown product of silicones used in construction.<sup>8</sup> Most importantly, TMS can also be formed inside the fabs from ambient HMDSO through acid-catalyzed reaction.

Chemical filtration has become a standard protective barrier to prevent process degradation and UV exposure tool lens contamination, as well as for general fab protection in photolithography environments. Most silicon-containing chemicals, such as siloxanes with two or more silicon atoms, are captured effectively by chemical filters, whereas TMS is not captured well by common carbon-based filter systems.

Common hybrid filtration systems used in photolithography optics protection use a mix of acidic, basic and/or neutral AMC adsorption media. In most cases, the mix is uniform in distribution throughout the filter systems or in some cases, acid layers are upstream, exacerbating the conversion of HMDSO to TMS. Filter lifetime performance evaluation becomes ambiguous if AMC test agents undergo reactions while passing through filter media.

## Experimental Approach

For the measurement of TMS and HMDSO at high concentrations, we employed a quasi-continuous monitoring system comprised of a gas chromatograph with flame ionization detector (GC-FID), cryogenic pre-concentration and a continuous inlet system. A dynamic dilution calibration system is also used for calibration and can employ liquid diffusion and injection sources of pure TMS and HMDSO, as well as a reactive source for TMS. For low concentration measurements in the parts per trillion range (ppt,  $10^{-12}$ ), we employed the method described by Lobert et al.<sup>9</sup>, which uses carbon-based trap samples followed by solvent extraction and GC-mass spectrometry analysis. Online gas chromatograph systems with photo-ionization detector (GC-PID) are used for the quasi-continuous monitoring of toluene.

For filter performance studies and product development, Entegris uses a versatile wind tunnel facility for the testing of full- and sub-size filters at various flow rates and with controlled temperature and humidity (Figure 1). This facility is capable of testing sub- and full-size filters at nominal flow rates, i.e., under real-world conditions. Temperature and humidity are maintained at levels typical for photolithography environments (22°C and 40%). Injection systems for liquid and gas-phase contaminants allow for variable concentrations of test contaminants between 10 parts per billion (ppb,  $10^{-9}$ ) and 10 parts per million (ppm,  $10^{-6}$ ). The most common test concentration is 1 ppm (1000 ppb) for accelerated lifetime tests and 30 ppb for low concentration challenges. Accelerated lifetime tests typically take between several days and four weeks.

The test facility also allows for testing filter stacks of up to five filters to accommodate filter sets as used in filter systems for the protection of exposure tools.

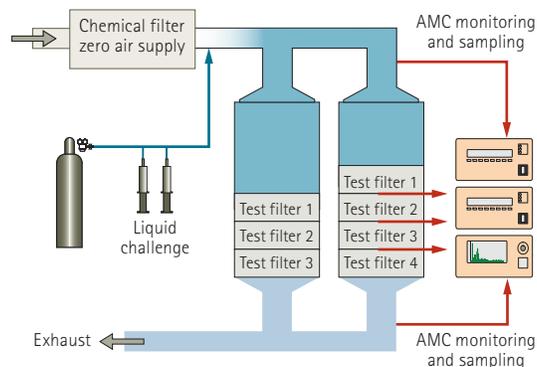


Figure 1. Portion of the wind tunnel facility and schematic of operation used to study chemical filter performance.

Liquid TMS and HMDSO with 99% purity were used for the calibrations in this study. Air streams used for the dilution and filter tests were purified using Entegris chemical filter systems such that AMC backgrounds were insignificant compared to challenge concentrations studied.

## Equilibrium and Conversion of HMDSO to TMS

HMDSO and TMS (Figure 2) exist in an equilibrium state,<sup>10</sup> which is governed by the presence of moisture (Eq. 1).



This equilibrium favors formation of TMS either in aqueous solution or with significant air moisture (40% RH). However, formation of TMS can be diminished by filtering out the HMDSO present in air (e.g., through recirculation and advanced chemical filters), which shifts the equilibrium to favor formation of HMDSO from TMS.

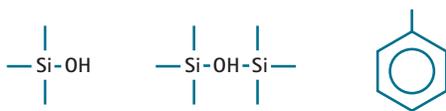


Figure 2. Molecular structure of TMS, HMDSO and toluene, filter test agents used for this study.

The initiation of the HMDSO breakdown in Eq. 1 also takes place in hybrid chemical filter media containing acidic layers or acid-coated carbon, and forms TMS, which is a low boiling point/low molecular weight AMC that propagates through a chemical filter array much faster than HMDSO.<sup>4</sup> The acid-catalyzed reaction appears to be much more efficient than the natural equilibrium.

Observations on high concentration (~25 ppm) systems found that the acid-catalyzed equilibrium favors the condensation of two molecules of TMS into one molecule of HMDSO when encountering acidic filter media.<sup>11</sup> However, such high concentrations cannot be found in lithography environments, where typical TMS concentrations are much less than 100 ppb, and those of HMDSO a factor 10 less than TMS.<sup>9</sup>

Tests in the Entegris wind tunnel facility clearly showed that the conversion of HMDSO to TMS on acidic media is consistent at low concentrations (less than 1 ppm). The near-quantitative conversion of HMDSO on acidic beds is actually used in our labs to create TMS challenge gases<sup>4</sup> that are employed for filter and media testing. The equilibrium concentrations of TMS and HMDSO on an acid bed were experimentally determined and are summarized in Figure 3. A source concentration of 180 ppb HMDSO, for example, yielded only 65 ppb HMDSO downstream of the acid chemical filter (green curve), whereas most of it (115 ppb) is converted to yield 230 ppb TMS. The HMDSO yield, however, increases at higher concentrations and it is conceivable that it is favored at very high TMS concentrations (>>1 ppm).

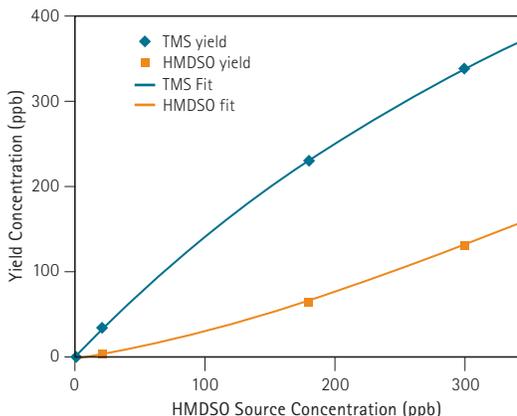


Figure 3. The yield of HMDSO and TMS when converting HMDSO on acidic media at concentrations below 1 ppm. TMS yield downstream is always higher than HMDSO yield.

TMS was always a product of HMDSO conversion and TMS concentrations were always higher than those of HMDSO. The condensation of two molecules of TMS into one molecule of HMDSO was not observed to be dominant at concentrations below 1 ppm.

Using the above experimental data to calculate that reverse reaction, how much TMS could be condensed into HMDSO below 1 ppm, yields HMDSO values of only 3–20% of TMS on the same acid media. Whereas this condensation may happen at the same time as our observed HMDSO breakdown, the resulting net conversion is that of HMDSO to TMS.

For the natural, uncatalyzed equilibrium, we calculate even lower yields for the formation of HMDSO from TMS. Concentrations up to 10 ppm of TMS should yield only 10 ppb of HMDSO and TMS at cleanroom levels of 1 ppb would not produce any significant amounts of HMDSO.

## Filter Testing with Toluene and HMDSO

### Advantages of Toluene as a Test Agent

The described conversion of HMDSO to TMS on acidic filter media poses a problem when performance testing of chemical filters is carried out with HMDSO instead of other, more inert compounds. Entegris promotes the use of toluene ( $C_6H_7$ , Figure 2) as a filter test agent because it is inexpensive, it is at the low end of the organics range that is targeted with chemical filter systems for exposure tools and, hence, represents a worst-case filter performance scenario, very similar to HMDSO. Toluene is also a common reference compound recognized by the ITRS and some OEMs and is the most common calibration compound for organic AMC detection. More importantly, it is non-reactive in most environmental settings relevant to photolithography and it does not adhere (“stick”) to surfaces of the test facility. Toluene is purged out of the wind tunnel system with clean air quickly and it does not cloud optical, analytical detection systems such as photo-ionization detectors.

Typical lifetime performance curves for toluene removal on a chemical filter system consisting of three hybrid media (acid/activated carbon) filters is shown in Figure 4. Toluene retains its integrity upstream and downstream of the filter set over long periods of time.

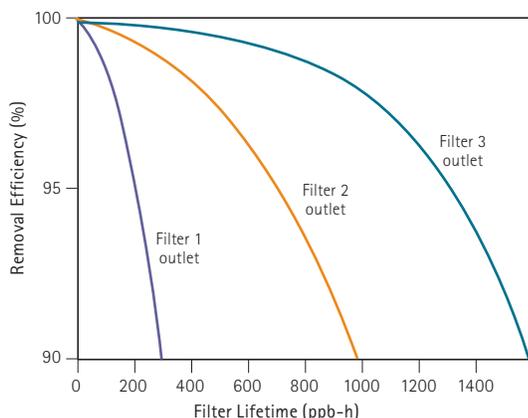


Figure 4. Smoothed toluene performance curves on a set of three carbon-containing AMC filters.

### Results from Using HMDSO as a Test Agent

Whereas toluene provides chemically conservative performance curves, HMDSO does not. Figure 5 shows the results of using HMDSO as a test agent when using acidic hybrid filter media. Entegris filtration systems for optics protection contains three filters in series (Figure 6a), creating two “interstacks” between filters 1 and 2, as well as between filters 2 and 3. “Inlet” is the upstream challenge before filter 1, “outlet” is the concentration downstream of the entire filter stack.

Panel (a) in Figure 5 shows the upstream HMDSO challenge concentration, which was maintained around 825 ppb. Upstream TMS concentration, mostly an impurity of the HMDSO used to create the challenge, was below 0.1 ppb, insignificant for the test purpose.

Panels (b) through (d) in Figure 5 show the TMS and HMDSO concentrations after filters 1, 2 and 3. Even though the upstream TMS challenge was zero, very high amounts of TMS were observed downstream of all chemical filters.

#### Filter #1

For the 825 ppb inlet challenge, which is equivalent to 1650 ppb of TMS, about  $548 \pm 59$  ppb of TMS is produced from conversion on the first hybrid filter (brown triangles in Figure 5b), a portion of 33% of the available silicon. Together with the unchanged HMDSO breaking through (blue squares), the upstream challenge concentration of silicon is reached after filter 1 at about 700 hours into the test (this is the steady-state point, where upstream and downstream concentrations are the same because of breakthrough).

#### Filter #2

The second filter outlet builds up TMS (red triangles in Figure 5c), and levels off at  $684 \pm 84$  ppb. Assuming that the HMDSO concentration of the first interstack at  $548 \pm 59$  ppb is the challenge to the second filter, and assuming furthermore that all of the produced TMS eventually passes through these filters largely unchanged, we can conclude that the second interstack adds at least another 157 ppb from conversion of first interstack HMDSO. That conversion would be 14% of the available HMDSO. Summing TMS and HMDSO (light blue squares) together, the upstream challenge concentration of silicon (about 825 ppb) is reached after filter 2 at about 1000 hours into the test.

**Filter #3**

Outlet data of the third filter showed  $694 \pm 105$  ppb TMS (orange triangles in Figure 5d), which had not leveled off yet and would have probably settled in around 800 ppb (extrapolated). HMDSO showed 330 ppb, which still significantly increased and had not yet leveled off at the end of the test. Outlet TMS would be a combination of TMS in the second inter-stack plus any new conversion, which is based on the ~500 ppb of HMDSO in the second interstack. That conversion is numerically only 1%, because concentrations were not fully leveled yet.

In addition, as mentioned previously in Figure 3, a portion of the TMS may have been converted back to HMDSO, numerically diminishing the TMS yield somewhat. The sum of TMS and HMDSO after filter 3 did not yet reach the original challenge concentration, confirming that the filter was not saturated yet. That steady-state would have been reached around 1200 hours into the test (extrapolated data).

**Steady-state TMS Concentration**

TMS concentrations leveled off at about 550 ppb, 680 ppb and 800 ppb (estimated). The leveling off of TMS concentration after each filter is mostly a function of conversion efficiency on the acid filter media. That means that the conversion reaches a steady-state, governed by the HMDSO challenge concentration as well as the availability of conversion sites (media density, granular structure and acid strength), flow rate, humidity and temperature. With flow, RH, temperature and available sites being constant in any one filter design, conversion of HMDSO to TMS diminishes from filter to filter, mostly based on HMDSO concentration. However, the cumulative amount of TMS at the outlet of the filter stack (800 ppb) equals a conversion of about 50% of the available silicon challenge (1650 ppb) once all filters are saturated.

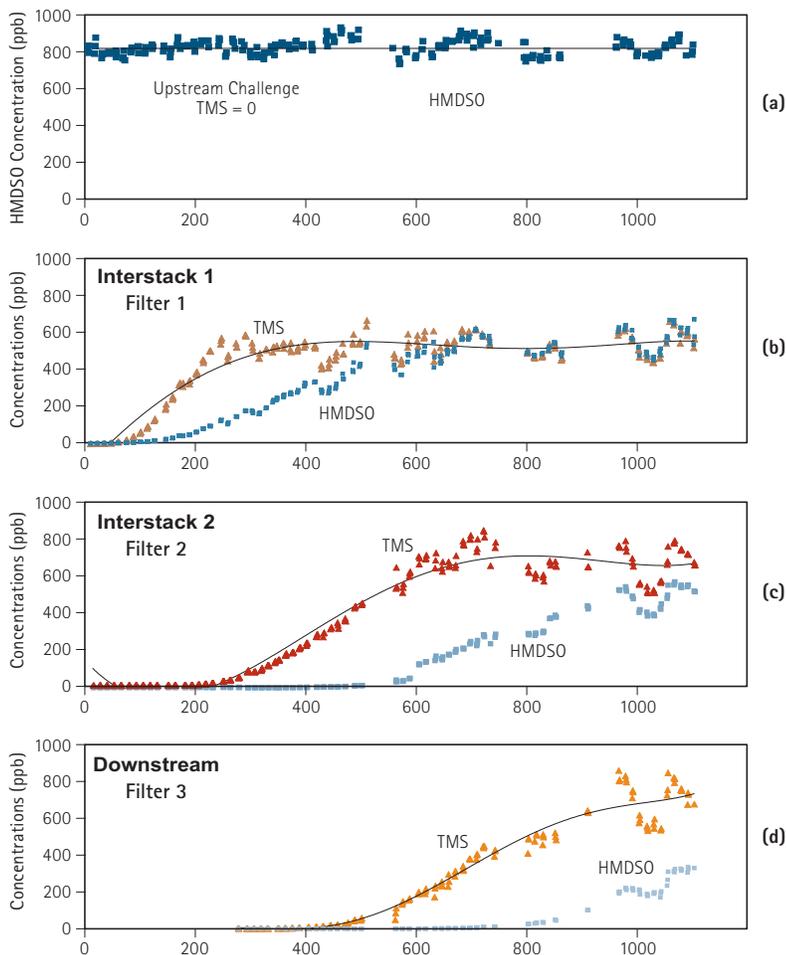


Figure 5. TMS production from HMDSO on acidic media.

### Impact on Filter Performance Estimates

The conversion of HMDSO to TMS theoretically should increase the lifetime estimate for HMDSO on the filter system, because the filter is challenged with less HMDSO and the TMS yield is not counted toward the lifetime. We found, however, that the resulting lifetime estimate for HMDSO was very similar to that of a parallel test with toluene as the challenge gas. This outcome, in effect, means that HMDSO is not as efficiently retained by the chemical filter media as expected, presumably because of the presence of TMS, which occupies the same active sites on the carbon media.

## Solutions to Prevent the Conversion of HMDSO to TMS on Chemical Filters

Figure 6a shows the filter design as used for the test in the prior section. Figure 6b shows a common filter design that uses the acid media upstream of the filter and which exacerbates the catalytic decomposition of HMDSO. That conversion of HMDSO to TMS can easily be prevented by employing an asymmetric filter design (AFD) as shown in Figure 6c. The asymmetric design 2 employs non-acidic carbon media in its first two of three

filters (or filter layers) and adds the acidic media to the end. This design still provides the necessary retention of ammonia and bases on its last filter, but prevents the conversion of HMDSO to TMS on its first or first two filters, as is the case in the uniform design and asymmetric design 1. This new asymmetric filter design 2 has been developed by Entegris for the use in tool filter systems for optics protection.

Note that TMS already present in air would migrate through any of the filter systems in similar fashion, regardless of the design of the filter system. Capture and retention of TMS in air (below 1 ppm) is only governed by the absolute amount of adsorptive media as well as the flow rate and TMS concentration, but not by the acid layer sequence.

HMDSO is not the only compound of interest that reacts on acidic media. Propylene Glycol Methyl Ether Acetate (PGMEA) is a common solvent used in photoresist applications and one of the most abundant organic chemicals found in lithography environments. PGMEA reacts on acidic surfaces to form, amongst others, acetic acid. Acetic acid is an undesired AMC and subject to acid control requirements by exposure tool OEMs. Preventing the formation of acetic acid is another benefit of the asymmetric filter design introduced here (patents pending).

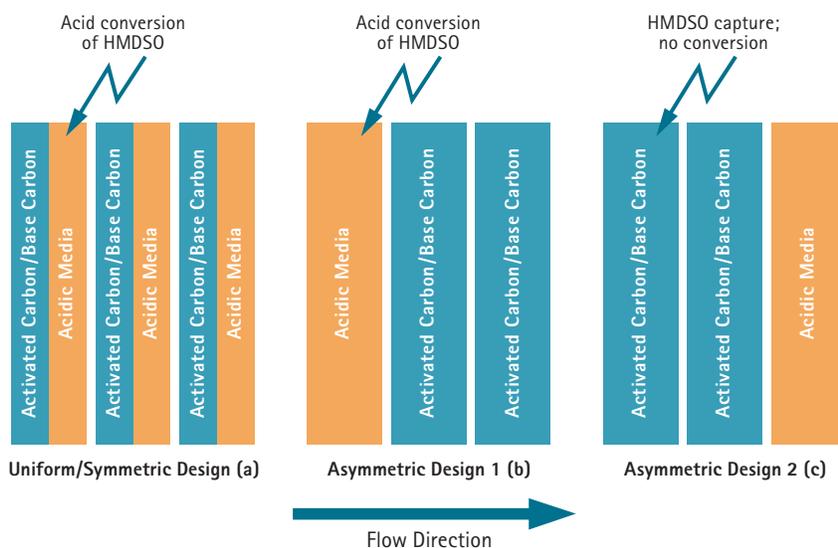


Figure 6. Schematic of (a) uniform mixed media, (b) an asymmetric design that causes the same conversions and (c) an asymmetric filter design which prevents acid conversions of organic compounds.

## Conclusions

We described the equilibrium conversion of HMDSO and TMS, particularly when encountering acidic chemical filter media.

A state-of-the-art wind tunnel test facility with the ability to vary AMC concentrations between very low and very high levels is required to fully understand dynamic chemical interactions between AMC challenges. Advanced analytical capabilities are required to measure all AMC with confidence at all concentrations.

We showed that HMDSO is converted to TMS on acidic surfaces at concentrations below 1000 ppb. The inverse reaction, condensation of TMS to HMDSO, does not contribute much at these concentration levels.

We clearly showed that HMDSO is an unsuitable chemical for testing chemical filter system life-time performance. HMDSO is reactive and requires interpretation of results. Toluene is a test agent that behaves conservatively and yields unambiguous results.

Avoiding contact of captured HMDSO with acidic media is suggested when designing chemical filter systems for optics protection in photolithography. The design of an asymmetric filter system with acidic media last in sequence was introduced for the use in optics protection applications.

## References

1. Matsumoto, Y. and Miyaji, A., *U.S. Patent 5,430,303 Exposure Apparatus*; July 4, 1995.
2. Fosshaug, H., Ekberg, M. and Kylberg, G., "Some aspects on mechanism responsible for contamination of optical components in DUV lithographic exposure tool," *Proc SPIE*, v. 5754, p. 1601-1628, (2005).
3. Kuntz, R.R., Liberman, V., Downs, D., "Experimentation and modeling of organic photocontamination on lithographic optics," *J. Vac. Sci. Technol.*, B 18, 1306-1313, 2000.
4. Grayfer, A., Belanger, F., Cate, P., Ruede, D., "New filter media development for effective control of trimethylsilanol (TMS) and related low molecular weight silicon containing organic species in the photobay ambient," *Proc. SPIE*, 6518, 651842-1 (2007).
5. The International Technology Roadmap for Semiconductors, ITRS 2009. [www.itrs.net](http://www.itrs.net)
6. Belanger, F., Cate, P., Grayfer, A., Petersen, R., Ruede, D., "Examination of the prevalence and abundance of noncondensable, nonreactive optical surface contaminants in the scanner environment," *Proc. SPIE*, 5754-200 (2005).
7. Grümping, R., Mikolajczak, D., Hirner, A.V., "Determination of trimethylsilanol in the environment by LT-GC/ICP-OES and GC-MS," *Fresenius J Anal Chem*, 361, 133-139 (1998).
8. Coleman, M. 1991. *Summary Report of Postflight Atmospheric Analysis for STS-26 to STS-36, SD4-91-430*, National Aeronautics and Space Administration, Washington, D.C.
9. Lobert, J.M., Miller, C.M., Grayfer, A., Tivin, A.M., "Measurement of low molecular weight silicon AMC to protect UV optics in photolithography environments," *Metrology, Inspection, and Process Control for Microlithography XXIII*, edited by John A. Allgair, Christopher J. Raymond, *Proceedings of SPIE Vol. 7272* (SPIE, Bellingham, WA 2009) 727222.
10. Protasova, L.V., Grinberg, E.E., Bessarabov, A.M., Makarov, V.V., Polyanskii, M.A., "The mechanism and kinetics of the synthesis of hexamethyldisiloxane," *Russian journal of physical chemistry*, 65 (2), 283-28 (1991).
11. Seguin K., Dallas, A., Weineck, G., "Semiconductor Filtration Technical Note CFTN-1-SC," Donaldson, February (2008).

This application note is a technical publication: Lobert, J.M., Cate, P.W., Miller, C.M., Ruede, D.J., Wildgoose, J.R., "Considerations for chemical filter performance for low molecular weight silicon AMC." *Proc. SPIE*, 7638, 7638110, 2010.

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