REVIEW

Field-induced and photon-induced CD degradation in transmission reticles: a comparative review

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Abstract. The progressive degradation of transmission reticles used in semiconductor production occurs via several mechanisms, the most prevalent being haze formation in 193 nm lithography. A less frequently observed yet more significant problem involves the migration of the chrome from the features in chrome-on-glass (COG) reticles onto the clear areas. All these critical dimension degradation mechanisms can result in yield loss but only the effect of haze can be corrected by cleaning the reticle. Chrome migration is caused by exposure to 193 nm UV and electric field. To differentiate between the two causes, different acronyms are used: here, PIM for photon-induced migration, and EFM for electric field-induced migration. The characteristics of both mechanisms are described and compared. A common explanation is proposed for PIM and EFM type 1, whereas EFM type 2 involves a physical process that is not present in PIM. These types of damage have only been observed in COG reticles to date, but the physical processes causing them are common to all materials. It is, therefore, concluded that ensuring the prevention of these progressive forms of reticle damage in all types of transmission reticle requires both the elimination of humidity and the exclusion of electric field from the reticle's environment. © *2022 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JMM.21.3.030901]

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1 Introduction

After the electric field-induced migration (EFM) of chrome in reticles was identified and given the acronym EFM in 2003,[1] a similar form of reticle degradation was found to be caused by 193 nm UV exposure in the lithography tool.[2,3] Both damage mechanisms cause transmission degradation resulting in yield loss through across-chip linewidth variation (ACLV), and this type of degradation can escape detection through routine reticle inspections. EFM can also ultimately progress to line bridging at wafer level if exposure of the reticle to electric field persists.

EFM had been observed before the advent of 193 nm lithography, but for several years it had been misdiagnosed as a form of electrostatic discharge (ESD) damage.[4] Research subsequently proved that although ESD and EFM are both caused by exposure of the reticle to electric field, EFM is unrelated to ESD and involves different physical processes. Procedures that are designed to prevent ESD in the semiconductor production environment are not always able to prevent EFM, and in some cases they actually make the risk of EFM worse.[5]

With the advent of 193 nm lithography, new forms of reticle degradation were encountered, the first of which was haze formation. Although haze had been a problem in previous generations of lithography, it became a serious problem for early adopters of 193 nm lithography, affecting both reticles and the optics in the lithography tools. The presence of water vapor was found to be a critical factor for haze formation, which led to most 193 nm lithography tools being purged with clean dry air. Similar extremely clean dry air (xCDA) purging systems were developed to keep reticles clean and dry during storage, and this effectively eliminated the 193 nm haze problem during the typical production life of a reticle.[6,7]

Around 2006, another form of reticle degradation appeared in 193 nm lithography, leading to ACLV and yield loss.[2] This type of damage, sometimes referred to as the "sun effect," produced

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*Address all correspondence to Gavin Rider, gavinrider@microtome.com a radial variation in the printed linewidth across the reticle, and it was found to be dependent on the accumulated exposure dose in the lithography tool. EFM was discounted as the primary cause since it was being found in dark-field via reticles, into which there is likely to be very little penetration of electric field. Chrome migration was eventually identified as the cause of the ACLV, and the conclusion reached was that the chrome migration was being caused by exposure to 193 nm radiation in the lithography tool. Further research showed that this form of reticle degradation could also be prevented by excluding water vapor from the lithography tool and the reticle's storage environment.[3]

2 Details of the Reticle Degradation Mechanisms

2.1 *Electric Field-Induced Migration*

The initial identification of EFM as a damage mechanism that is distinctly different from ESD came after retrospective analysis of hundreds of atomic force microscope (AFM) images of test reticle features that had been deliberately damaged by exposure to electric field in a research program at International Sematech.[8,9] Analysis of the way the electric field interacts with the conductive features in the reticle pattern revealed a previously unobserved dependence of the damage characteristics on the locally modified field strength and its polarity between the reticle features. Two different damage characteristics were observed:

a. EFM type 1: At the onset of degradation, with the lowest level of local electric field strength, a meniscus was seen to form at the interface between the chrome features and the glass substrate. Once this process had started, its rate of progression appeared to be independent of both the local field strength and its polarity, leading to the deduction that the electric field acted like a "switch" to turn on the process, but it did not actually drive the movement of the material. This form of damage was attributed to the field-initiated surface diffusion of neutral chromium atoms. This deduction was supported by the findings from other research into the effect that an electric field has on surface atom mobility in solid metals.[10]

b. EFM type 2: With a slightly higher level of electric field present between the reticle features, the formation of a protrusion on the edge of the chrome line was observed. The rate and the direction of protrusion growth were found to be dependent on the strength, polarity, and the direction of the local electric field, indicating that this process involved the migration of positive chromium ions.

These interpretations were consistent with all the observed damage characteristics in the AFM images from Sematech's field-stressed test reticles, but the explanation that solid chromium could be made to move at room temperature in this way was doubted by many. Therefore, an experiment was carried out to reproduce the observed effects under tightly controlled conditions, in which the field strength between the reticle features could be accurately known and any current flowing within the reticle could be measured.[11]

A test reticle was constructed that allowed the conditions present in the earlier field-exposure tests to be reproduced through the direct application of voltage to the test reticle features rather than by exposing the reticle to an external electric field. The geometry of the test cells, which was designed to create identical field configurations and electrical resistance in the gap areas of all the test cells in the reticle, is shown in Fig. 1. Cells containing features with line widths and gap spacings between 1 and 5 μm were tested. The current flowing between the features was automatically recorded as the voltage was varied by the test probe apparatus, allowing the surface conduction in the reticle to be studied and also to confirm that no ESD had taken place.

This fairly simple experiment revealed that surface conduction in the reticle included a nonohmic component that increased significantly as the voltage between the features was increased. The nonohmic component of the surface current was larger when the central electrode, which has the highest field strength generated at its surface due to the geometry of the test cell, was biased positively. This confirmed that the surface conduction involved positive charge carriers that were being generated at the edge of the positively biased electrode by the strong local electric field. The nonlinear current characteristics are shown in Fig. 2.

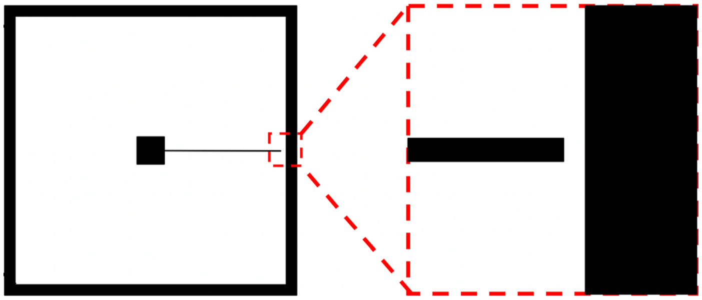


Fig. 1 Design of the test cells in the reticle used to quantify EFM. Dark areas are the chrome features and white areas are clear glass. Variable voltage was applied to the test cells using an automated probe station designed for testing electronic devices, and the current flowing at each voltage step was recorded into a digital file for offline processing.

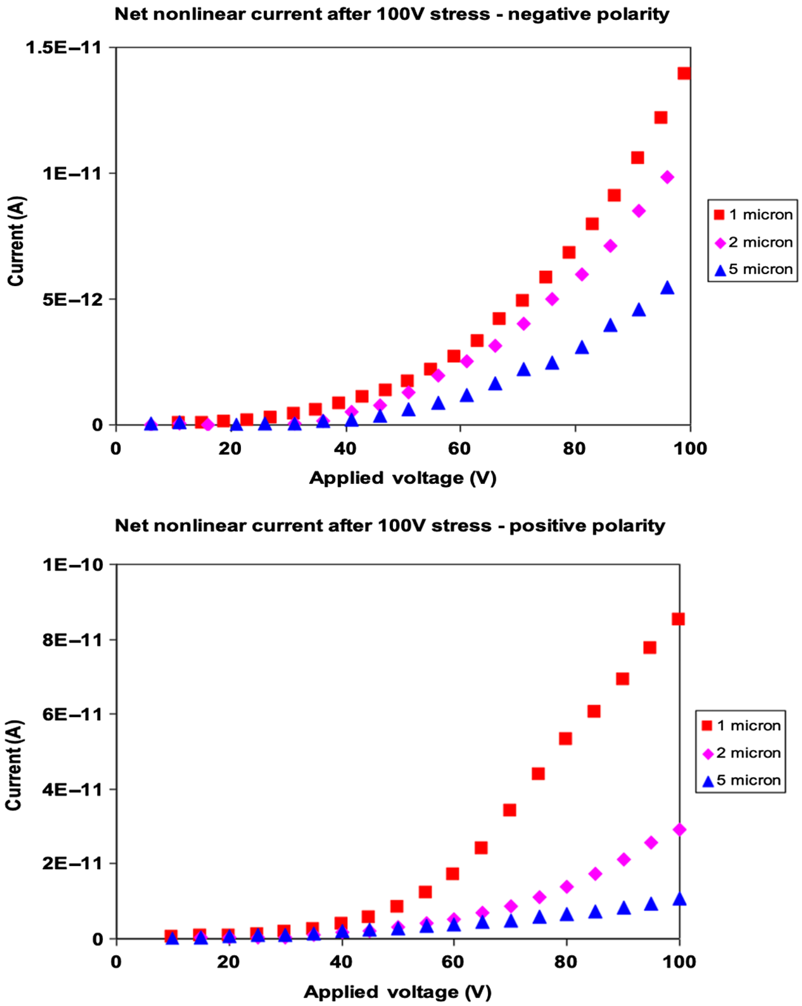


Fig. 2 Net nonohmic current flowing in the test reticle with positive and negative bias applied to the central electrode. Results from test cells with 1, 2 and 5 μm line width and gap spacing are shown. The ohmic component of the current has been subtracted to reveal the nonohmic characteristics. Note the significantly larger nonohmic current flowing when the central electrode was positively biased.

Fig. 3 AFM images of a test reticle feature damaged by EFM, from the experiment reported in Refs. 11 and 12. The line width and gap spacing are 1 μm (vertical scale in the perspective view is ×10 for greater clarity).

Following publication of these initial experimental results, the test reticle was imaged using the same AFM that had been used in the earlier field-exposure experiments at International Sematech. The images of the damaged reticle features, some of which are reproduced in Figs. 3 and 4, confirmed all the previous interpretations of the damage mechanisms of EFM and provided very clear evidence of the stages of degradation that a chrome-on-glass (COG) reticle would undergo as a consequence of being exposed to an electric field.[12]

Physical evidence is clearly present in the higher magnification AFM images of the gap region, as shown in Fig. 4, to indicate that chromium has migrated on the glass surface of the reticle all the way to the opposite electrode, reinforcing the deduction from the earlier current/voltage analysis that chromium ions played a part in the surface current flowing in the reticle. A complete description (and interpretation) of all the damage characteristics observable in these images is given in the original publication.[12]

Around the same time as the results of this experiment were published, another research group identified a case of EFM that had caused ACLV in a production reticle, resulting in yield loss despite the reticle having passed all its routine inspections.[13] Migrated chrome was found on

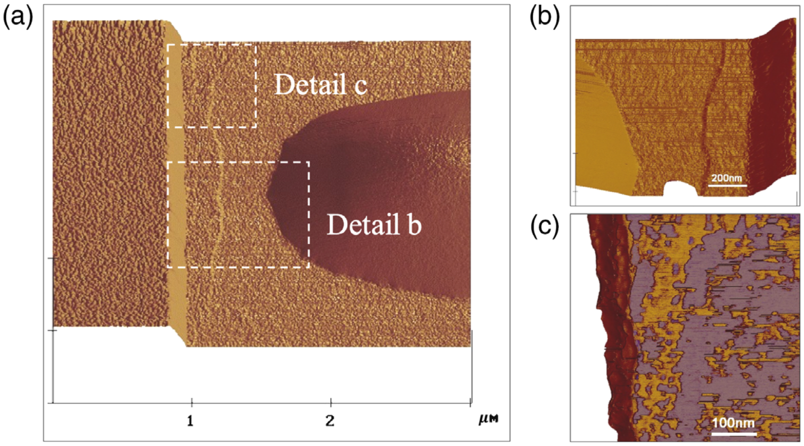


Fig. 4 Magnified views of the gap region of the test structures shown in Fig. 3 clearly showing a film of chromium building up against the second electrode after migration across the gap from the positively biased chrome line. The discontinuous part of the film in region *c* has been emphasized by tinting the areas between the image contrast contours using photoshop.

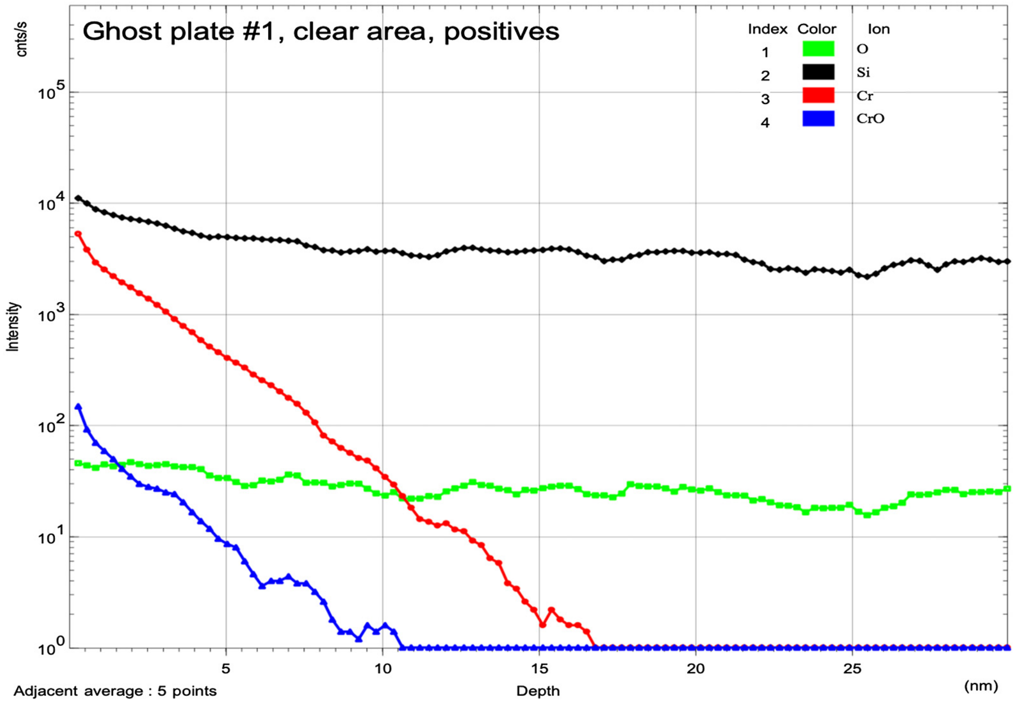


Fig. 5 Time-of-flight secondary ion mass spectrometry analysis of clear area of the reticle analyzed in Ref. 13 that exhibited reduced transmission, causing ACLV (private communication of data obtained by the Grenon consultancy). The transmission reduction was identified as having been caused by chrome migration through EFM.

some clear areas of the reticle, reducing the transmission in the affected areas, and leading to ACLV in the printed wafers. The role that EFM had played in the reticle's degradation was confirmed by time-of-flight secondary ion mass spectrometry (Fig. 5), which was capable of detecting tiny amounts of chromium on the affected clear areas. No other routinely available analytical method used in a semiconductor production facility would have had the surface sensitivity and spatial resolution to be able to confirm this, which possibly explains why EFM is rarely being detected and reported from production facilities today. It simply cannot be found by standard reticle inspection methods.

2.2 *Photon Induced Migration*

The first report of 193 nm photon-induced chrome migration in a reticle used in a production facility was by Tchikoulaeva et al. in 2008.[2] It had been known for a long time that reticles could be degraded by haze formation as a function of the reticle's accumulated exposure dose, but after the conditions leading to haze formation had been controlled some exposure dose-dependent mask degradation remained. This was detected after the introduction of routine ACLV monitoring as part of the wafer manufacturing process. The degradation was found to exhibit a dome-shaped distribution across the reticle, being most severe in the center, and also to be stronger in reticles having a higher proportion of clear areas in the pattern.

Checks were carried out to identify whether haze or any other form of contamination could have played a part in the ACLV. Back-side cleaning and pellicle replacement did not correct the problem, and while front-side cleaning did result in a small improvement, the original critical dimension (CD) signature of the reticle could not be retrieved. The CD variation was attributed to dimensional changes of the reticle features, rather than to variation in mask transmission, although this interpretation is open to question since the CD measurement was carried out using an aerial image metrology system tool, so the CD reading would be sensitive to transmission variation in the same way as the lithography process. Tchikoulaeva et al. did not have access to the transmission mapping tool used in Ref. 13.

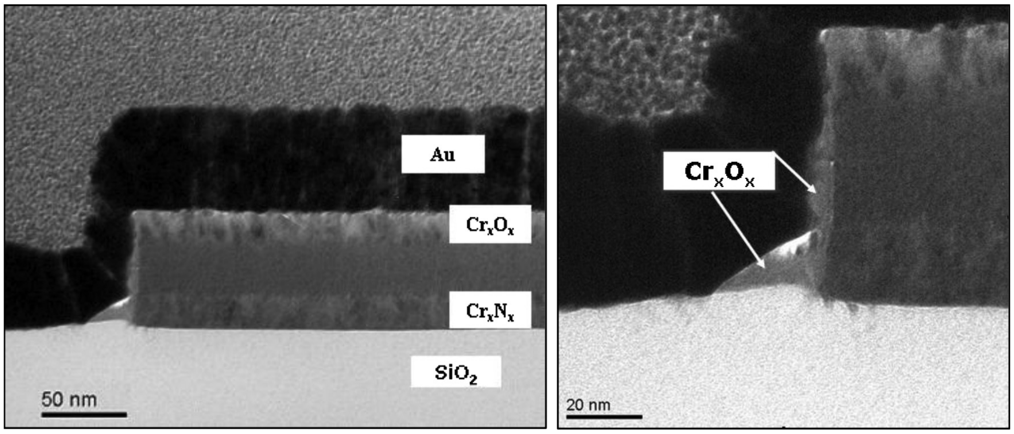


Fig. 6 Transmission electron microscopy of a cross-section through a degraded reticle feature showing consumption of the chromium on the side-wall to form oxide and the formation of a chromium oxide "footing" at the junction with the glass, reproduced from Ref. 2 (the gold overlayer is part of the TEM sample preparation).

Transmission electron microscope (TEM) analysis of new and degraded reticles indicated that chromium oxide was growing on the side-walls of the features in the reticle, and a "footing" of chromium oxide was also forming at the base of the chrome line, as shown in Fig. 6. The equivalent features in the newly manufactured reticle had been shown to be perfectly clean, so this change had occurred during reticle use. Scanning electron microscope (SEM) inspection of other structures in the reticle showed that smaller features were more susceptible to the degradation than larger ones, but no explanation for this was given (see later comments in the discussion section). There was no firm conclusion about the mechanism behind the CD variation and Tchikoulaeva et al.'s paper concluded with a statement:

> "Experiments reproducing the degradation are required to describe the mechanism behind this problem in detail."

Shortly afterward, a study of this effect was published by Bruley et al.,[3] in which they carried out just such an experiment as had been proposed by Tchikoulaeva et al. They investigated backside reticle haze as a possible cause of the CD variation seen in their wafers, but in accord with the results of Tchikoulaeva et al., they found that the CD deviation was not corrected after cleaning the mask. SEM analysis of their degraded reticles showed the growth of a similar "footing" of chromium oxide at the base of the chrome line to that reported by Tchikoulaeva et al., and they also observed the formation of small "droplets" on the glass surface in a via reticle as shown in Fig. 7. The degradation in their reticle had advanced further than in the reticle studied by

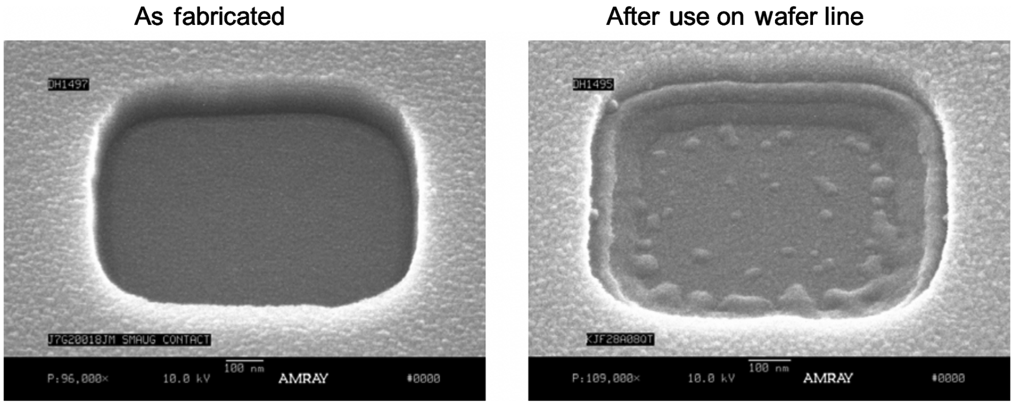


Fig. 7 Formation of a "footing" of chromium oxide at the junction with the glass in a production reticle, plus the formation of droplets within the clear area of the via opening, reproduced from Ref. 3.

Tchikoulaeva et al. This image confirms that the transmission of the reticle would have been degraded by the migrated material, as had been found in Ref. 13 at a much earlier stage of reticle degradation, and that the ACLV would not have been entirely due to dimensional changes of the reticle features as had been concluded by Tchikoulaeva et al.

It was noticed by Bruley et al. that the production reticles suffering most strongly from CD degradation had been randomly allocated to different lithography tools depending on the tools' availability. Some of these tools were being purged with humid air while others were purged with clean dry air. By restricting reticle use to one or other of the tool sets, a reduction in the rate of reticle degradation was seen. Therefore, it was concluded that humidity cycling played a significant part in the degradation process. To study this phenomenon more closely, a special test chamber was constructed that could be used to expose a reticle to precisely controlled atmospheric conditions while UV doses equivalent to reticle use on a production line were applied. It was confirmed in this way that humidity cycling produced the greatest rate of CD degradation.

It was also noted that in the case of their via reticles (which have small open areas in an otherwise continuous chrome film, as shown in Fig. 7), the CD degradation was greatest in isolated vias than in areas of the reticle containing grouped vias. This behavior appears to be contrary to that found by Tchikoulaeva et al., who reported that the CD degradation was greatest in reticles with more open areas in the pattern. Clearly, there are some aspects of this degradation mechanism that were not yet fully understood by those reporting it, and these will be considered in the discussion section.

Bruley et al. based the interpretation of this phenomenon on the chemistry of chromium, which can form compounds with different valency, CrVI being the most strongly oxidized and highly reactive form. Their hypothesis was that 193 nm UV exposure caused the formation of strong oxidants on the clear areas of the reticle (O_3 and H_2O_2) that would react with the chromium, ultimately forming CrVI compounds that would then be highly mobile and migrate onto the glass surface. Unfortunately, no research has been performed that could identify the chemical state of the film during its formation, so this theory cannot be verified.

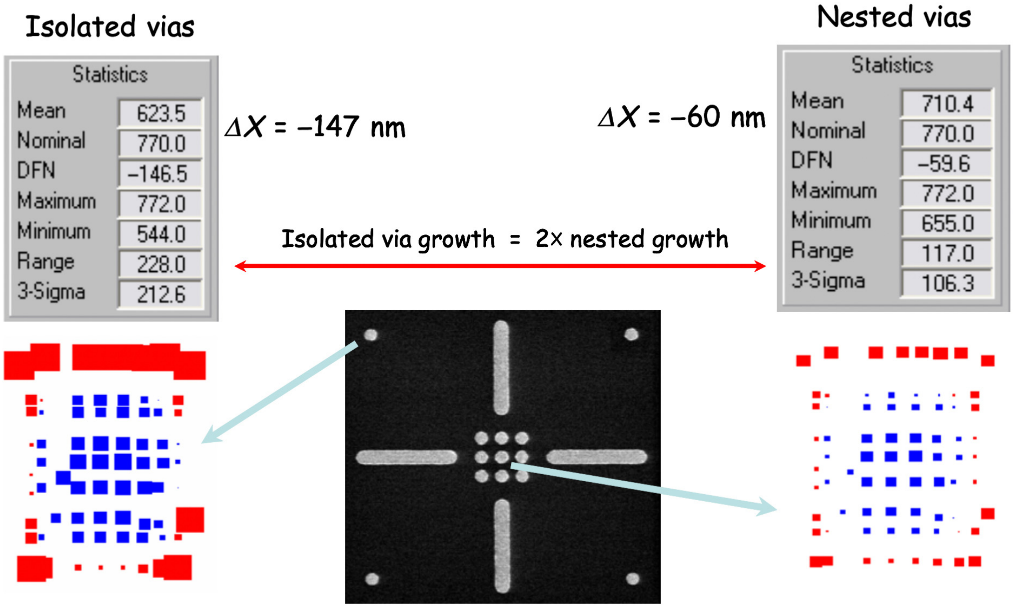
Both sets of authors concluded that the degradation process is complex and probably involves several contributory factors. Bruley et al. confirmed that their own experimentation had reproduced the EFM results of Ref. 11 with as little as 3 V applied between reticle features, but they discounted the role of electric fields in the generation of photon-induced migration (PIM) as it affected via reticles, which do not suffer from enhanced field induction in the same way as reticles containing isolated conductive features. However, the important roles played by humidity and UV exposure dose were confirmed.

3 Discussion

The similarities between EFM type 1 and PIM are noteworthy. Both processes result in migration of chrome (or other chromium-containing compounds that are ultimately detected as chromium oxide) onto the clear areas of the reticle. Such migrated chrome-containing films have been proven to affect transmission, and this affects the printed feature size. Different rates of degradation occurring in different parts of the reticle are revealed by the appearance of ACLV at wafer level.

The reason for this variation in degradation rate across a reticle is not always clear, however. In the case of EFM, it is known to arise from the variation of field induction as a function of the position within the pattern area. The details of the reticle pattern are dominant factors affecting field induction, which makes it impossible to generalize quantitatively about the risk of EFM to all reticles, but field induction is strongest around the periphery of a die image that has a continuous chrome border around it.[14] This distribution pattern was seen in the analysis conducted by Labovitz et al. of a degraded production reticle,[13] supporting the interpretation that the transmission loss and the chromium migration detected in their analysis was caused by EFM.

In PIM, the variation of severity across the wafer seems to have different contributory factors. Tchikoulaeva et al. reported that the CD degradation was strongest in the center of the reticle. Their analysis indicated that the heating of the reticle under UV illumination in the scanner would be up to 0.5°C greater in the center of the reticle than around the edges. While this could play some part in enhancing the rate of chrome migration, it seems unlikely that a temperature



Isolated vias

Statistics

Mean	623.5
Nominal	770.0
DFN	−146.5
Maximum	772.0
Minimum	544.0
Range	228.0
3-Sigma	212.6

Nested vias

Statistics

Mean	710.4
Nominal	770.0
DFN	−59.6
Maximum	772.0
Minimum	655.0
Range	117.0
3-Sigma	106.3

Fig. 8 Variation in the rate of CD degradation as a function of a via opening's local environment, from Ref. 3. Nested vias degrade more than 2× slower than isolated vias.

difference of only 0.5°C could cause such a significant variation in the CD degradation rate as was observed in their production reticles. Bruley et al. also described a similar radial variation in the rate of degradation, but curiously the figure in their paper purporting to illustrate it does not actually show the effect that they describe in the text. Their figure, reproduced here in Fig. 8, shows that the CD of isolated vias degrades faster than that of nested vias. There was no further reference made in the body of the paper to this observation, so this characteristic of PIM remained unexplained.

Tchikoulaeva et al. reported that the degradation rate was greater in reticles having more open areas in the pattern, which seems to conflict with the characteristic described by Bruley et al. Neither Tchikoulaeva et al. nor Bruley et al. proposed any explanation for this variability of the degradation rate as a function of the structure of the reticle pattern, but for PIM to be properly understood such characteristics need to be explained.

Since the physical characteristics of EFM type 1 and PIM seem to be remarkably similar, generating similar "footings" at the junction of the chrome with the glass substrate, photon-stimulated surface diffusion of chrome atoms would seem to be the most plausible explanation for PIM.

It was already determined during the initial analysis of the characteristics of EFM type 1 that the growth rate of "footings" at the base of a reticle feature was not directly related to the local field strength, which would be highest at the corners of the conductive features. In EFM type 1 the observed footings were smaller at the corners, as shown by the AFM image of one of the test reticle structures from International Sematech's reticle damage research program, reproduced in Fig. 9 (the vertical scale of this image is magnified ×10 for greater clarity). The distortion of the line by EFM type 1 has been emphasized by tinting the affected areas red. Since the distribution of the line broadening by EFM type 1 could not be explained by the local field strength, it had to be explained by some other factors. Uniform outward diffusion of chrome from the line onto the glass surface once a threshold field strength has been reached accounts for this characteristic, and an explanation for this is shown in Fig. 10.

As can be seen from the explanation in Fig. 10, a uniform outward flux of atoms from the chrome line would produce non-uniform line broadening, with a lower rate of "footing" formation at convex corners of the line, in accordance with the AFM imagery of features damaged by electric field exposure. If we compare this explanation with the characteristics of PIM described by Tchikoulaeva et al., we find a correlation. Their observations identified that smaller features, particularly resolution enhancement features added to the pattern, were affected more strongly than larger ones. This was illustrated by the SEM image reproduced in Fig. 11.

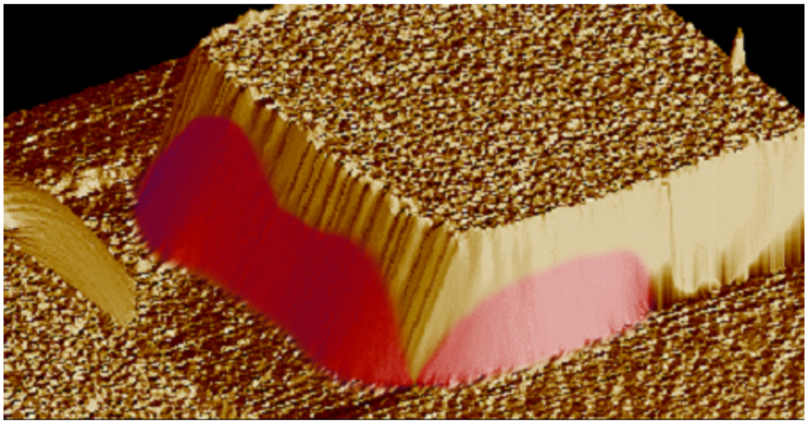
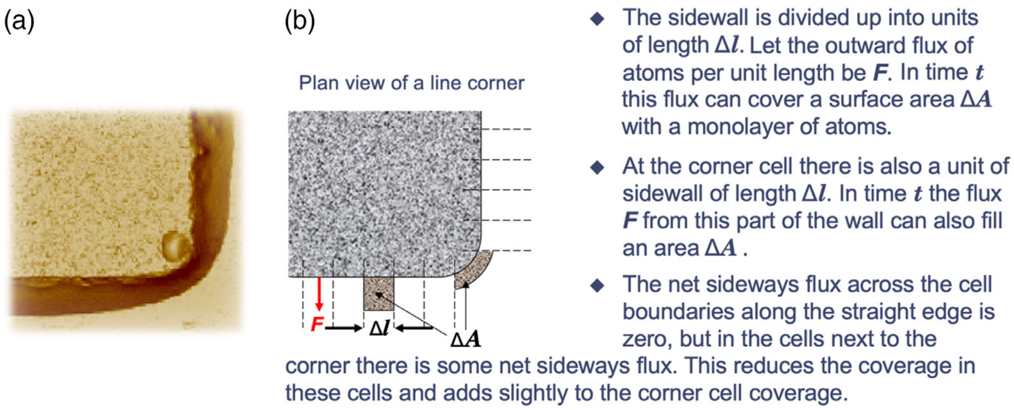


Fig. 9 Perspective AFM view of a reticle feature damaged by EFM type 1 after exposure to electric field. The “footings” formed at the base of the chrome feature are not present at the corners where the local electric field strength would be highest, indicating that the rate of footing growth is not driven by the field strength (vertical scale ×10).



- The sidewall is divided up into units of length Δl. Let the outward flux of atoms per unit length be F. In time t this flux can cover a surface area ΔA with a monolayer of atoms.
- At the corner cell there is also a unit of sidewall of length Δl. In time t the flux F from this part of the wall can also fill an area ΔA .
- The net sideways flux across the cell boundaries along the straight edge is zero, but in the cells next to the corner there is some net sideways flux. This reduces the coverage in these cells and adds slightly to the corner cell coverage.

Fig. 10 An explanation for the variation in the rate of line spreading by EFM type 1, based on a uniform diffusion flux outward from the line edge (part of the initial analysis of EFM from 2002, previously unpublished). (a) An AFM image of the corner of a reticle feature damaged by EFM type 1, and (b) an explanation for the variable amount of line spreading in this corner area.

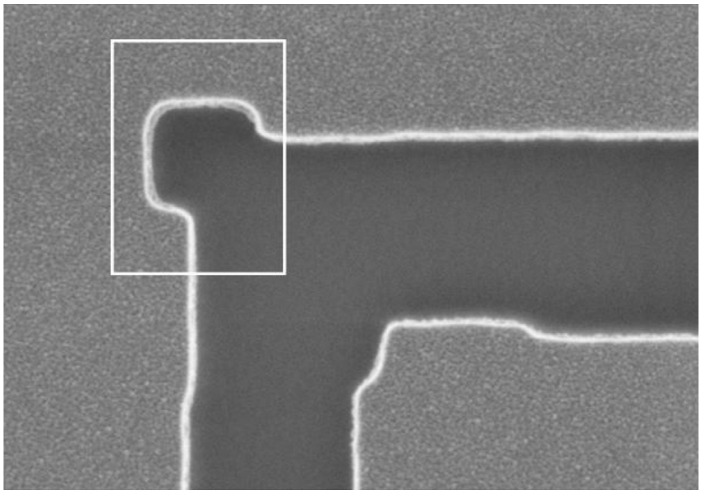


Fig. 11 SEM image of a production reticle incorporating resolution enhancement features that exhibit accelerated degradation by chrome migration (boxed area), from Ref. 2.

In their nomenclature, the feature they refer to is actually a clear area in the pattern, and what we can observe from their SEM image is that the growth of the "footing" is greater at the concave corners of the resolution enhancement feature (the opposite effect to that seen at convex corners, as shown in Fig. 10). This supports the interpretation that the line spreading under PIM is similar to that under EFM type 1, and results from a constant rate of outward migration of chrome atoms from the line edge onto the glass substrate.

The experiments of Bruley et al. indicated that CD degradation in nested via holes was less than in isolated ones, so how does the theory of the surface diffusion of chrome explain this? It can be understood in the same way that the variability of the line broadening was explained in Fig. 10.

Surface atoms, even in solid metals, are constantly moving at room temperature and exchanging places with their neighbors, a phenomenon that has been observed using atomic resolution microscopy of a copper surface.[15] The rate for surface copper atoms to exchange places was estimated to be around 10^8 Hz. The probability of a surface atom "hopping" into a neighboring surface site is a function of temperature, which drives the thermal vibration of surface atoms at a frequency in the terahertz range at room temperature. The rate of lateral diffusion is also a function of the number of vacant lattice sites that a surface atom can move into Ref. 16, and on a typical metal film in a reticle, which in crystallographic terms is highly imperfect, there will be plenty of such sites available. Surface diffusion on a reticle absorber film is seen to be a highly probable event.

On a typical solid surface in the absence of any perturbation there will be equal diffusion in all directions, resulting in no net alteration to the surface morphology. In the case of EFM type 1, wherein a perturbation is applied to the surface by an electric field, the field strength first reaches the point where it can enhance atomic mobility at the sharp edges of the film in contact with the substrate. The enhancement of the field strength at the junction of the metal with the glass is shown in the computer simulation of Fig. 12. Thus, enhanced diffusion first occurs at the base of the chrome lines when the local field strength exceeds the EFM activation level, forming the familiar meniscus at that junction. Under conditions resulting in EFM type 2, the electric field strength is higher and reaches this threshold value over the entire surface of the reticle feature, imparting a preferred direction for atomic diffusion that results in the morphological changes to the surface and to the macroscopic structure that are shown in Fig. 3.

In PIM, the mobility enhancement of surface atoms will occur mainly at the illuminated vertical edges of the absorber film (since the major surface of the absorber film that the light strikes is in contact with the glass substrate, so atomic mobility at that interface will be constrained, by comparison with that at a free surface). Every vertical surface will therefore experience the outward diffusion of mobile surface atoms, leaving behind a surplus of vacant sites into which atoms diffusing from the rest of the absorber film can migrate. This will produce a net

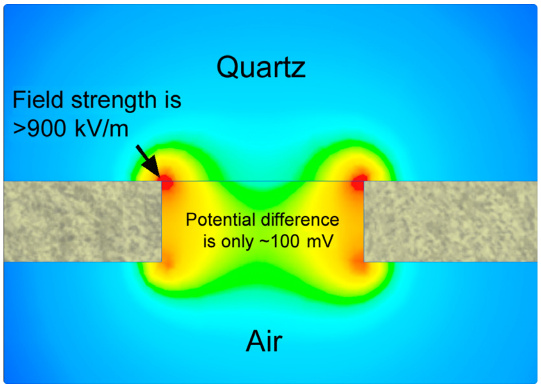


Fig. 12 Computer simulation of the local field strength in a reticle exposed to an externally applied electric field. The local field strength is seen to be the highest at the point where the metal is in contact with the substrate, owing to the polarizability of the quartz. Thus, this is the first point to be degraded by EFM, creating a meniscus or "footer."

movement of mobile surface atoms toward the apertures in the chromium film and then outward onto the glass surface.

With an isolated via that is surrounded on all sides by a large area of intact absorber film, there is a large reservoir of mobile surface atoms available to replenish any surface vacancies created by outward diffusion of chromium atoms onto the glass. So, an isolated via opening will maintain a high rate of outward diffusion as the "lost" surface atoms will be efficiently replaced. In the case of nested vias, the reservoir of mobile surface atoms that can replenish the vacant surface sites being created at the via openings will become depleted, since there are more outlet points per unit area for diffusing atoms to be lost from the surface than is the case with isolated vias. This simple consideration explains the reduced rate of outward diffusion of chrome atoms onto the glass with nested vias than is the case for isolated vias, as reported by Bruley et al. (Fig. 8).

Tchikoulaeva et al. also reported CD degradation in reticles having linear features, where the degradation was seen to be greater in more open areas of the pattern. To explain this we have to consider the "free energy" of the exposed surface (this is essentially the potential energy stored in a surface due to the surface atoms not being completely surrounded by bonds with their neighbors). A surface will naturally try to achieve a state of minimum free energy, which means minimizing the number of "dangling bonds" at the surface. This is why liquids form droplets that have a minimum surface area. Solids cannot easily achieve minimum surface energy by changing their shape in the same way as liquids (although this is indeed what happens during EFM type 2) but they can achieve partial relaxation by adsorbing other materials from the atmosphere. This is why glass surfaces will readily adsorb a thin film of water molecules—because it reduces the surface's free energy.

This free energy consideration dictates whether liquids will wet surfaces, and it also determines whether one material will be miscible in or bond with another. It was found during the experimentation into EFM that the contact angle of chromium diffusing onto glass is extremely shallow—around 10°—which indicates that it is energetically favorable for chromium to be on a glass surface. The surface with chromium on it has lower free energy than a clean glass surface. The morphology of migrating chrome in a reticle after receiving field stress in the EFM experiments of Ref. 12 is shown in the AFM line profile scans of Fig. 13, illustrating the very shallow contact angle created by the meniscus that is formed by EFM type 1.

Atomic diffusion will be random (to a first approximation) after a neutral chromium atom is liberated onto the glass surface. However, a net directional movement will be imparted by the varying surface density of the migrating species and by the change in surface free energy that the adatoms create. There will be a net movement away from glass areas with a high chromium density into areas with lower density. This achieves density-driven redistribution and reduces the surface free energy of the quartz substrate. Thus, in a reticle pattern having large clear areas, there will be a strong influence on the amount of surface diffusion taking place, because the chrome atoms will rapidly spread onto the clean glass surface to reduce the surface free energy. It is the corollary of the situation described between isolated and nested vias—one case is dominated by the availability of mobile chromium atoms to replace those lost from the metal surface,

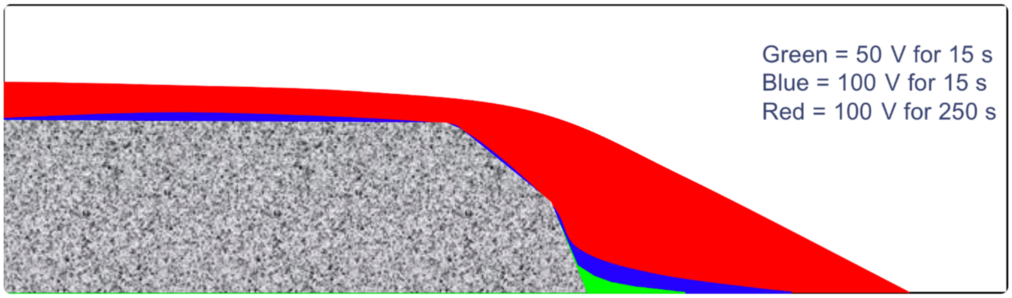


Fig. 13 AFM line profiles of a reticle feature distorted by EFM under various stress conditions, from the research described in Refs. 11 and 12. The contact angle of the meniscus formed by EFM type 1 is around 10 deg (the gray area is the original line profile).

whereas the other is driven by the availability of unoccupied space on the glass into which chromium atoms can diffuse.

The free energy consideration also explains the formation of chrome droplets or islands, as shown in Figs. 3 and 7. It is seen to be energetically favorable for droplets to form if the concentration of migrating chrome atoms reaches a certain limit (just as water droplets will start to form and create mist if the concentration of water vapor in air exceeds the solubility limit).

If both EFM type 1 and PIM are a consequence of the enhanced surface diffusion of chromium atoms, it seems reasonable to believe that localized temperature variations could result in a variable rate of line spreading. So, the radial temperature variation indicated by the thermal modeling of Tchikoulaeva et al. could account for radial variation in the CD degradation that they observed. However, the 0.5°C difference in temperature across the reticle indicated by their thermal simulation model is unlikely to result in a significantly different rate of diffusion, so how can the variation observed in production reticles be explained?

The side of the absorber film in direct contact with the substrate, which is illuminated by the laser, is chromium nitride as shown in Fig. 6. This material acts as an antireflection coating, to suppress any reflections within the reticle and the optics of the lithography tool illumination system that might compromise the illumination uniformity. The photon energy absorbed into this layer is converted into heat that then dissipates throughout the bulk of the reticle. Over an extended exposure period, the bulk of the reticle will be heated in the nonuniform way indicated by the thermal modeling of Tchikoulaeva et al., but the heat being generated at the absorber film will be much more intense and the local temperature will rise considerably higher than the volume-averaged temperature indicated by the simulation.

The energy is first deposited into a film that is <100 nm thick, and then the heat is conducted away into a glass substrate that is more than 6 mm thick. It seems inevitable that the temperature of the absorber film will rise considerably higher than the 1.5°C average temperature rise indicated for the bulk of the reticle by the thermal modeling program. The variation in the temperature across the absorber film is also likely to be proportionately greater than the indicated 0.5°C value, so the observed radial variation in the rate of reticle degradation can reasonably be interpreted as a possible thermal effect.

The final point to discuss is the observation that reducing a reticle's humidity controls the degradation by PIM, and whether it will similarly help in the control of EFM. A possible explanation for this characteristic can be found in the studies of supported chromium oxide catalysts.[17] Although the conditions found in the typical applications for chromium as a supported catalyst are somewhat extreme by comparison with the conditions to which a reticle is normally exposed, some of the observations relating to chromium's chemistry are relevant to how reticles may behave. It is reported that chromium catalysts supported on silica substrates strongly bond with the hydroxyl groups ($-OH^-$) that are present on a hydrated silica surface under ambient conditions, ultimately displacing the hydroxyl groups from the surface and replacing them with chromium oxide. Thus, the presence of hydroxyl surface species would appear to act as an attractant for migrating chromium, thus enhancing the diffusion rate for chromium on quartz under hydrated surface conditions (or conversely suppressing it under dehydrated conditions).

In an alternative theory, Bruley et al. considered the photon-induced migration of chrome to be driven by a chemical reaction involving the oxidation of the chrome by strong oxidants (O_3 and H_2O_2) produced by the UV light's reaction with adsorbed water molecules on the reticle surface. They hypothesized that hexavalent chromium oxides formed in this way would be more highly mobile on the surface of the reticle than compounds having a lower oxidation state. So, it was proposed that by preventing the oxidation of chromium through this photochemical reaction, the migration could be controlled.

The image of the degraded via opening in Fig. 7 shows significant growth of a ring of oxide on the side-wall immediately above the footing, a characteristic that was also noted by Tchikoulaeva et al., so this seems to support the theory of chromium oxidation taking place under UV irradiation. However, the sidewall oxide and the footing are seen to be distinctly separate entities in both the TEM image of Fig. 6 and the SEM image of Fig. 7, so the oxide formed on the sidewall through a UV-stimulated reaction does not appear to be the same material that subsequently migrates to form the footing and ultimately the surface droplets shown in Fig. 7. The sidewall oxide and the footing appear to have separate origins and to be distinctly different from one another. Thus, it seems to be indicated by the TEM image of Fig. 6 that chromium oxide formation and chromium migration are driven by two separate mechanisms, rather than the migration being driven by the photochemical reaction as proposed by Bruley et al.

Hence, hydroxyl-enhanced surface diffusion is considered more likely than the model proposed by Bruley et al., to explain the greater rate of reticle degradation under hydrated conditions and the suppression of PIM by keeping the reticle surface dry. The role apparently played by humidity cycling as reported by Bruley et al. is more difficult to explain, and this would probably require further experimentation to be performed with reticles, in a similar way that supported chromium catalysts have been studied.

4 Conclusions

Electric field-induced and 193 nm photon-induced migration of chrome in COG reticles can both be understood as an enhancement of surface diffusion that occurs naturally in metals at room temperature. The reported characteristics of PIM have been interpreted as due to surface diffusion that is driven by the density of mobile atoms on the chrome surface, the availability of free sites on the quartz surface into which they can migrate and the surface free energy associated with those sites. EFM has two different forms: EFM type 1,which has been interpreted as field-induced surface diffusion of the kind that occurs in PIM, and EFM type 2, the field-driven diffusion of chromium ions that are generated by the strong electric field produced at the edges of reticle structures when the reticle is exposed to an external electric field.

The rate of migration in all cases will be dependent on the relative free energy levels of the chromium and quartz surfaces. Since adsorbed water vapor on silica or quartz creates surface hydroxyl species with which chromium reacts strongly, chromium diffuses more readily on a hydrated surface than on a dry surface. It is observed that by reducing the humidity of the quartz surface, the rate of reticle degradation by PIM can be reduced to a level that is tolerable in semiconductor production. It follows that the same should be true when considering EFM type 1 and some of the transmission degradation of the substrate caused by EFM type 2.

However, the images of Fig. 3 and the line profile scans of Fig. 13 clearly show that significant structural changes occur to the features in a reticle under EFM type 2, and these changes will not be affected by the hydration state of the quartz substrate. The surface of the chrome line becomes smoother due to the filling of surface defects by migrating chromium atoms, and this reduces the antireflection quality of the surface.[8] The shape of the chrome line also changes significantly under electrostatic stress. Humidity control is unlikely to be an effective preventive measure against these characteristics of EFM type 2, so the only way of preventing such damage will be to exclude electric fields from the reticle's environment.

These damage mechanisms have been observed in COG reticles, but to date have not been reported in reticles made using other absorber materials, such as MoSi.[18,19] However, it would be imprudent to believe that such degradation mechanisms are necessarily restricted to COG reticles since the physics and chemistry underlying the processes that cause them are common to all materials. It is, therefore, recommended that measures should be adopted in the storage, handling, and operating environments of all transmission reticles to fully exclude electric fields and to eliminate humidity. The relevance of the described phenomena to the reflection reticles used in EUV lithography is uncertain, but the same protective measures are likely to be appropriate for the protection of EUV reticles.

References

1. G. Rider, "EFM: a pernicious new electric field-induced damage mechanism in reticles," in *SEMATECH ESD Symp.* (2003).
2. A. Tchikoulaeva et al., "ACLV degradation: root cause analysis and effective monitoring strategy," *Proc. SPIE* **7028**, 702816 (2008).
3. J. Bruley et al, "Cr migration on 193 nm binary photomasks," *Proc. SPIE* **7272**, 727215 (2009).
4. J. Wiley and A. Steinman, "Investigating a new generation of ESD-induced reticle defects," *Micro Mag.* **17**, 35–40 (1999).

5. G. Rider, *How to Protect Reticles from Electrostatic Damage*, SPIE Press, Bellingham, Washington (2018).
6. O. Kishkovitch et al., "A practical solution to the critical problem of 193 nm reticle haze," *Proc. SPIE* **6730**, 67301A (2007).
7. W. Goodwin et al., "More on practical solutions to eliminate reticle haze and extend reticle life in the production environment: specially designed RSPs, internal POD purifiers, and XCDA purged reticle stockers," *Proc. SPIE* **6924**, 69244N (2008)
8. J. Montoya, L. Levit, and A. Englisch, "A study of the mechanisms for ESD damage to reticles," *IEEE Trans. Electron. Packaging Manuf.* **24**(2), 78–85 (2001).
9. A. C. Rudack et al., "Induced ESD damage on photomasks: a reticle evaluation," *Proc. SPIE* **5256**, 1136–1142 (2003).
10. T. M. Mayer et al., "Electric field induced surface modification of Au," *J. Appl. Phys.* **85**, 8170 (1999).
11. G. Rider and T. S. Kalkur, "Experimental quantification of reticle electrostatic damage below the threshold for ESD," *Proc. SPIE* **6922**, 69221Y (2008).
12. G. Rider, "Electric field-induced progressive CD degradation in reticles," *Proc. SPIE* **7122**, 71220G (2008).
13. S. Labovitz et al., "Detection of progressive transmission loss due to haze with Galileo mask DUV transmittance mapping based on non-imaging optics," *Proc. SPIE* **7122**, 712216 (2008).
14. G. Rider, "Reticle ESD module 1; electrostatic field simulation," in *SEMATECH Reticle ESD Workshop* (2003).
15. R. Van Gastel et al., "Nothing moves a surface: vacancy mediated surface diffusion," *Phys. Rev. Lett.* **86**(8), 1562–1565 (2001)
16. C. Ratsch and M. Scheffler, "Density functional theory calculations of hopping rates of surface diffusion," *Phys. Rev. B* **58**, 13163 (1998).
17. M. A. Vuurman et al., "Characterisation of chromium oxide supported on Al_2O_3, ZrO_2, TiO_2 and SiO_2 under dehydrated conditions," *J. Mol. Catal.* **80**, 209–227 (1993).
18. I. Servin et al., "Aging study in advanced photomasks: impact of EFM effects on lithographic performance with MoSi binary and 6% attenuated PSM masks," *Proc. SPIE* **7823**, 78230N (2010).
19. H. Razman et al., "Characterization of electrostatic discharge threshold voltage of phase-shift mask reticle," *Int. J. Electr. Comput. Eng.* **12**(2), 1265–1273 (2022).

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