

New type of haze formation on masks fabricated with Mo-Si blanks

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ABSTRACT

In our paper we make an analysis of conditions for the haze development on photomask fabricated on Mo-Si containing substrates. We bring in focus cases of haze formation on masks with intrinsically very low contaminants level and being exposed in very well controlled atmosphere. There are clear indications that this new type of haze formation deviates from the generally accepted models not only with respect to the formation mechanisms but also with regard to the chemical composition of the haze products. In our analysis we speculate that the new haze type formation is closely related to the earlier reported CD degradation observed on Mo-Si masks [2]. We also analyze the hypothesis that the ingredients for the haze formation are not only airborne contaminants and/or traces on the mask surface, but are also provided by the substrate material. Finally we present and discuss experimental data in the view of the advanced models.

Keywords: Haze formation; ammonium sulphate; molybdate; MoSi materials; haze formation mechanism; crystal growth.

1. INTRODUCTION

Haze formation remains one of the main root causes for mask failure in the wafer fab. This is also one of the most investigated mask degradation topics (compare e.g. to the amount of reports on CD degradation of the masks). Despite considerable research and investigations conducted by industry and research laboratories the ultimate mechanisms of haze formation remain unclear. There were proposed different reaction chains which lead to haze formation [1, 2]. In most of the cases, however, the argumentation is limited to the analysis of the possible chemical reactions and their thermodynamical stability. It is only seldom that material related aspects are involved in the definition of the mechanisms for haze formation[1, 3].

Although any kind of mask can be affected by haze, the most enticing haze formation mechanisms and properties are encountered on Mo-Si based materials (MoSi from now on) under the illumination with 193 nm. This is not only because the radiation energy is high enough to promote all kind of interesting chemical and physical phenomena (e.g. O₂ or H₂ ionization, complex modes of surface diffusion), but also because typically the masks for this type of technology are very clean, i.e. exhibit a low amount of contaminants upon leaving the mask house.

In our paper we report on the inorganic haze formation which takes place under “extremely clean” conditions, i.e. low contamination level on the mask and in the wafer fab. We focus on MoSi based materials and masks illuminated with 193 nm. Based on our data and making a detailed analysis of the recent report we present a phenomenological analysis of the haze formation and also propose possible haze formation mechanisms.

2. HAZE DESCRIPTION

The typical inorganic haze defects do usually show quite large structures, sometimes in the order of μm and very often with well defined crystallographic facets [...]. By contrast, the type of the haze we investigate in this paper exhibits defects which are usually very small – largest structures are ~ 100 nm, but most of them do show sizes in the range of 50 – 100 nm, see Fig. 1. This type of haze occurs on 2 distinct places: top of MoSi material, see Fig. 1a, and structures side walls of the, see Fig. 1b-c. The defects grow seldom in size up to a few microns and they never built well defined crystallographic facets, independent on their final size.

In general affected masks show a tremendous amount of defects: sensitive enough inspection tools would trigger at each dot-like defect shown in e.g. Fig. 1a. Hence the inspection of the masks cannot be properly terminated and the

tool reports an overflow after only a few inspected swaths. The inspection throughput is dependent on the inspection mode, however, see Fig. 1d. The magenta dots indicate where the tool triggered a defect. If the mask is inspected in Transmission and Reflection mode then an overflow is encountered much earlier than if the mask is inspected in Transmission only, see Fig. 1d. This is because the defects on the side walls are extremely small and often hidden by the structure itself or stretch along the feature with not so much growth into the clear (as shown in Fig. 1c). It is important to mention though that very often the masks show haze on the structures walls only and nothing can be found on the areas covered with MoSi. In such cases a typical starlight inspection will even not detect any haze defects and the mask will be reported as being clean.

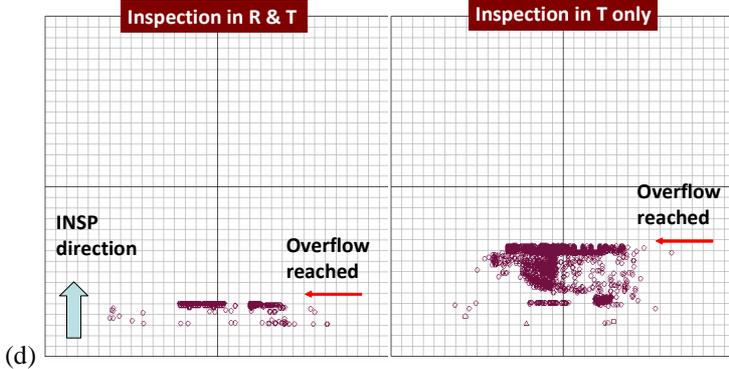
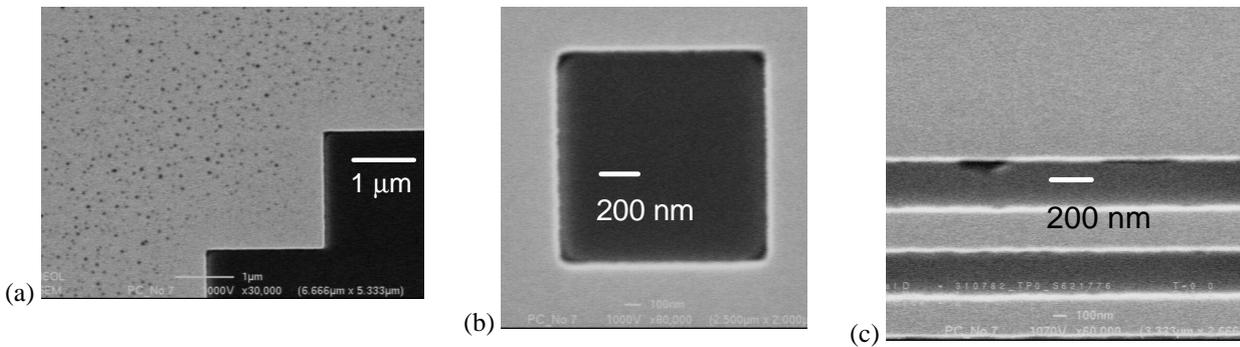


Figure 1 Haze can be found on top of MoSi material (a), but it also occurs on the structures side walls: (b) contact hole with haze (c) haze occurring on the side wall of a line and space structure. Inspection maps of inspected masks with haze in R&T and in T only (d).

One can speculate that the clustering of very small defects, occurring on the side walls and top (where available), might lead to the formation of larger defects. In majority of the cases the defects occur only on the side walls of the structured or would have a varicella-like distribution on top of MoSi as shown in Fig. 1a. If exposed to an energetic bombardment with electrons the defect will “evaporate” until completely disappear. We consider this as a confirmation for their aqueous state.

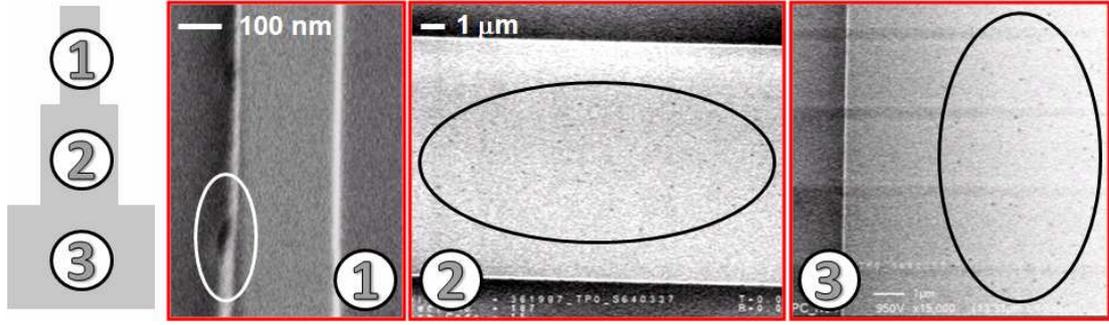


Figure 2 Schematics of a structure which consists of MoSi blocks of different areas. SEM snapshots taken on the respective structure from areas with different MoSi coverage.

An interesting observation was made with respect to the position on the mask where haze is usually found. While there is no preferential structures type triggering the haze formation, its occurrence is found to be a direct function of MoSi coverage. This can be easily seen in Fig. 2. It shows the schematics of a certain design feature composed of three distinct blocks of increasing MoSi coverage. It can be seen that if the dark area is large enough one can find a very large density of haze defects. The defect density will decrease once the MoSi coverage is reduced and there will be almost no haze product found for a feature which has a CD below 1 μm (Fig. 2 SEM 1).

The SEM snapshot from the thin structure in Fig 3 shows no visible black dots on the top, but there can be clearly seen a defect at the features side. Since the height of a structure is less than 70 nm while, in this particular case, the CD ~ 200 nm it can be easily concluded that haze occurrence on the features side is not only determined by the availability of the MoSi surface: this is an indication that the mechanisms of haze nucleation and growth on structures top and their side walls are distinct.

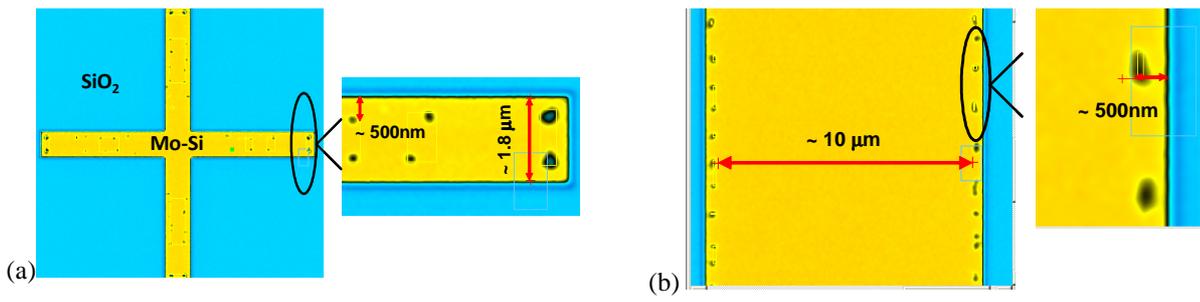


Figure 3 Haze occurrences at fixed distance from the feature edge: structure consisting of 1.8 μm line (a) is similarly affected as large bulky lines of 10 μm (b).

Figure 3 shows a very enticing property of the haze discussed here. While not easily found on each hazed masks, very often the haze occurs at a fixed distance from the feature edge. This typical range is ~ 500 nm and it stays constant on all features within an affected mask. Also this 500 nm scale is constant over the mask and from mask to mask. This edge haze can be only barely visible in SEM pictures since 500 nm from the features edge is where the electron emission in SEM is highest and no contrasts can be distinguished. That is why it can be captured only in the inspection pictures as are the ones in Fig. 3 made with NPI 5000 + inspection tool from Nuflare which proved to be exceptionally sensitive to this kind of defects.

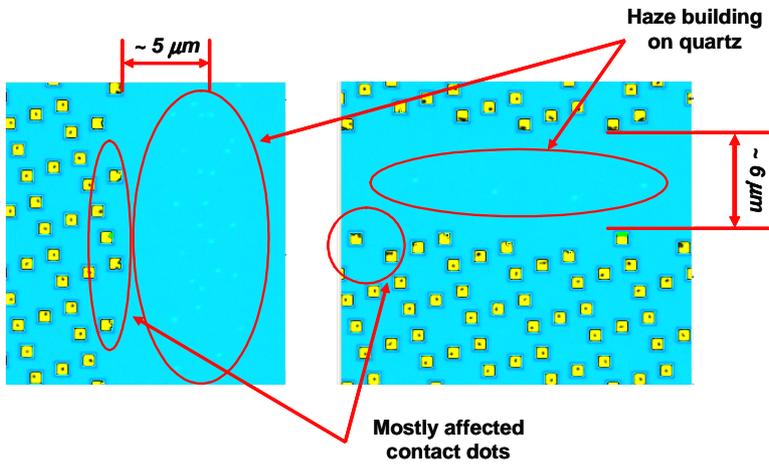


Figure 4 Haze on quartz and contact dots. It can be hardly detected with SEM. Dots facing large quartz areas are heavily affected by haze.

Until now we focused on presenting haze defects on MoSi structures. Indeed in all cases the inspection tools trigger the defects only on the absorber or the features side walls. The small defects on quartz, if any at all, are invisible with SEM. However, after a detailed review of the defect images generated by the inspection tool, one could find plenty of cases when haze is visible on quartz as well. Figure 5 shows large quartz areas affected by haze. Note also that the

contact dots will be differently attacked depending on their position with respect to the large quartz areas: the dots in immediate proximity will have large defects whereas dots which are far off the large quartz area will be less affected. On the significance of this observation will be further elaborated in the discussion part.

3. MATERIAL ANALYSIS

Since analytical tools have a spot size around 1 μm a chemical compositional analysis of such defects is rather difficult. For large enough defects Raman spectroscopy proved to be successful and deliver good data. However for the defect size shown here the main problem is not even the analytical spot size, but that the defects cannot be located via standard alignment techniques and hence the spot cannot be directed on the structure to be analyzed.

Alternatively, especially for the case shown in Fig. 1a one could analyze a large population of such defects and if a good signal to noise ratio is available an indication of the defects nature can be obtained. In such cases one could use FTIR or Ion Chromatography. In our case we applied the second approach.

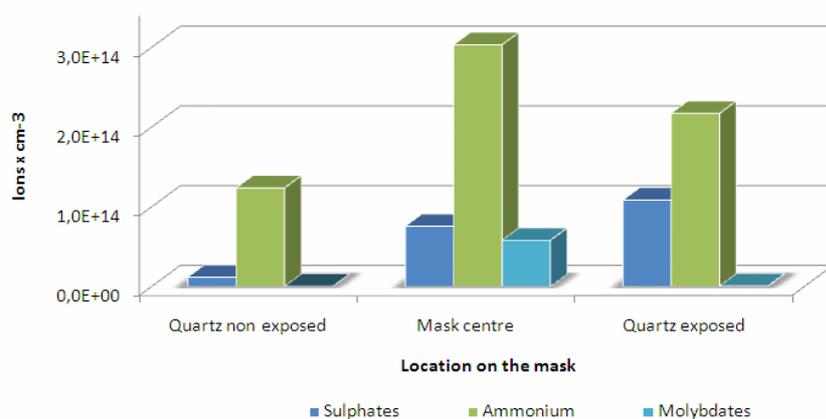


Figure 5 Main components detected on a mask which shows haze formation. Different areas on a mask are shown.

The used approach was local estimation of the ionic composition. For this droplets of water were used to wash out different areas on mask with their ulterior analysis for the ion composition. Thus we analyzed the ionic content of the pure quartz in the non exposed area, mask centre which encompasses solid features and clear and quartz only in the exposed area. The results are cast in Fig. 5. One can see that overall there is an increased level of ammonia which is however higher in the illuminated area. A different picture can be observed for the sulphates: while very low in the non illuminated area their amount increases for the mask parts which are under exposure. Interestingly enough, the ammonium amounts less on quartz than centre of the mask, but an inverse trend is observed for the sulphates. This is a clear indication that the type of defects present on quartz are actually different (or at least can be treated so) than the centre of the mask (which is a mixture of MoSi and quartz).

The ionic analysis reveals a high concentration of molybdates detected in the mask centre. Compared to non exposed masks, their concentration was found to be factor 9 higher (data not shown here). Note that the presence of molybdates and their relation to haze formation saw a scarce treatment in the literature and hence most of the formation models omit their presence. In our discussion part we dedicate a detailed analysis of possible contribution of the molybdates to haze formation.

4. DISCUSSION

Summarizing the results one can conclude the following:

- Haze occurs at preferential sites on the mask: on MoSi area, on side walls of the structures and on large quartz areas;
- Large defects form seldom;
- Several length scales of haze occurrence could be identified;
- While always present on the structures side walls, the top of large MoSi structures or quartz areas are selectively affected;

- Defect analysis revealed that ammonium and sulphates show increased values in the exposed area, but their ration is opposite for the exposed mask or quartz only;
- Molybdates are detected.

Based on these facts, in what follows, we will try to elaborate on possible haze formation mechanisms.

4. 1 Length scales and occurrences

Figure 6 summarizes the haze occurrence on MoSi films which could be observed on nearly all affected masks. Generally one can define five length scales.

At the distance R_1 from the edge haze will be always found. On our masks this magnitude never exceeded 500 nm, but could be lower than this. At the same time this magnitude stayed constant within a mask. We think that this magnitude is electromagnetic field (i.e. illumination) induced. The ingredients necessary for building this haze structure might have a similar source as the defects occurring on the side walls since only these two types of defects are always found on the mask, even then when no haze is detected on the large MoSi areas.

As already mentioned and confirmed by numerous images in the previous section, for the haze on large MoSi structures a critical amount of MoSi area is necessary in order to form defects which are detectable by inspection tools or SEM. One can only speculate that haze forms always, independent on the available MoSi amount, but it is simply not always large enough to be visible. It may be true or not, what can be always observed on the failed masks is if structures a smaller than a size range R_2 – no haze is detected (besides edge haze and on the side walls) and if the structures are larger than R_2 – visible haze will always form. These magnitudes vary among the masks, but remain always constant within a mask. R_2 is usually in the range of micrometers.

A fourth magnitude is R_4 which we postulate to be a function of R_2 and R_3 . It indicates a haze free zone on those structures which are large enough to provide conditions for haze formation. This magnitude is clearly visible in Fig. 1a and Fig. 2. It is also in μm range, usually below 5 μm , and can vary among the masks, but remains constant within a mask. It is tempting to consider R_4 also field related. If this is true, possible justification for the haze free zones would be some surface waves destroying the haze defects. This would, however imply (i) no defects would form at R_1 distance too and (ii) this magnitude would be constant for all affected masks. Both do not hold for our masks, however, which is an indication that fields do not play a role here. Instead the existence of R_4 is an evidence of a critical amount of MoSi is required in order to form visible defects; the surface availability toward feature end becomes scarce and hence no formation of defects is possible.

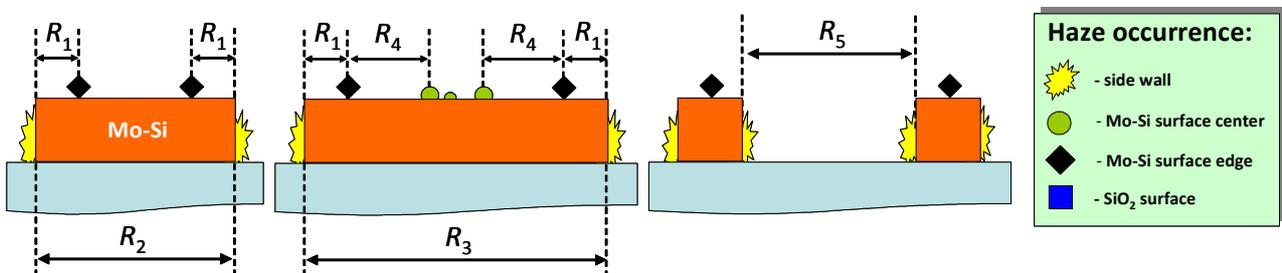


Figure 6 A schematics of where haze can be found on masks. The results are expressed in five length scales characteristic for the defects formation.

Haze formation on the side wall of the structures is an exciting phenomenon as well. First, it forms always and much faster than on any other mask location. No constrain to the amount of MoSi seems to be necessary. If the haze would be only material promoted than there is no explanation why micrometers of MoSi are required to form visible haze on the top of the structures and only a few nm (~ 70 nm thick are most of the MoSi layers) are enough for large and dense haze defects to be formed on the side walls and hence no photoeffects are expected. Second, if assuming the light has a promoting effect (e.g. photochemical reaction) then the electromagnetic field intensity is actually lowest at the structures walls. The only remaining explanation is that haze on the side walls is always present because a large reservoir of contaminants is available and beneficial conditions favour defect growth.

Before elaborating on this hypothesis we would like to refer to the defects which are found on quartz. A detailed analysis, as for the defects on MoSi, is difficult to be made, since the defects on quartz are almost impossible to detect;

the inspection tools will even not trigger at these defects. Nevertheless, it seems a typical scale R_5 exists here too, which is the minimum amount of quartz needed for “visible” haze to be formed. From our images this scale is in micrometer range as well and it is comparable to R_2 . Still, obviously the structures which face different amount of quartz area are distinctly affected by haze too. A very fortunate example was shown in Fig. 4 where contact dots are placed adjacent to quartz areas of different sizes: those dots which face large quartz areas are heavily affected by haze and it is clearly seen that dots facing reduced quartz areas are less affected. Again, the light might play a role, but it is most probably an indication that quartz participates directly into the supply of contaminants needed for haze building and this is independent where the defects finally occur: MoSi or quartz itself.

4.2 Reactants sources for haze

Interestingly enough, Fig. 5 shows that ammonium concentration in the centre of the mask is considerably higher than on quartz (both exposed areas). This leads to the conclusion that the presence of MoSi favours the retention or catalytic reaction leading to NH_4^+ formation. The substrate itself can be envisioned as an additional source for these ions.

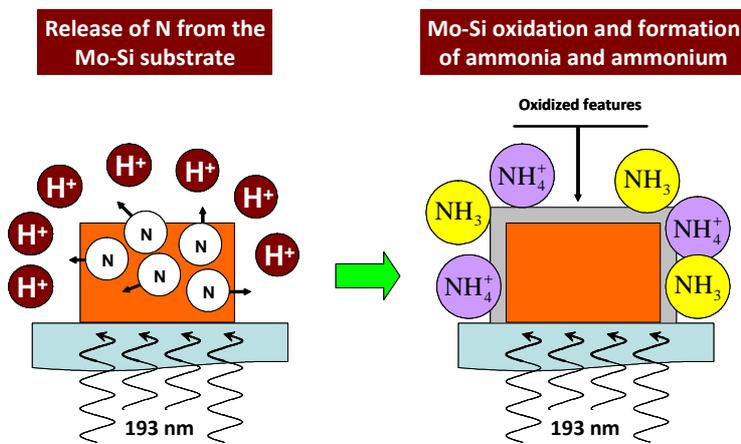


Figure 7 Alternative source of ammonium than airborne. Nitrogen release from the substrate, under extensive illumination with 193 nm.

MoSi layers do usually contain quite a high amount of nitrogen. The ratio of this element in the bulk will strongly depend on the material type and blank manufacturer. The MoSi layers are usually non stoichiometric layers. It is expected that under illumination the nitrogen will be released from the substrate and will diffuse towards the surface. Also under the action of the illumination H_2 can be easily ionized (dissociation energy is ~ 4.5 eV which is well below the photon energy of the 193 nm). Nitrogen from the substrate and ionized hydrogen from the atmosphere will build ammonia and ammonium ions and most part of it will be found on the surface. The schematic of this process is represented in Fig. 7. A similar mechanism was proposed by Yang et al. [4]. In their paper the authors experimentally confirmed the loss of nitrogen from the MoSi layers. The authors in Ref. [4] claims the oxygen concentration on the absorber layer increases upon illumination, i.e. a feature oxidation will take place. Similar observation was made by Faure et al. [5]. The authors showed TEM images of X-sections of MoSi features after long exposures. Indeed the features presented a thick film of oxide which encapsulated the whole structure. All these confirm that the MoSi layers are an important source of ammonia which directly contributes to the haze formation.

Detected sulphates can be found in a higher concentration on quartz than mask centre and non-illuminated quartz, as Fig. 5 shows. Since the substrate cannot be considered a source for sulphates, these ions are provided by the environment.

The retention rate of ammonium and sulphates ions seems to be strongly dependant on the substrate. Indeed in Fig. 5 it could be seen that the sulphate level is higher on the (non) illuminated quartz than the mask centre and the opposite holds for ammonium ions. If we assume the following ration between the areas:

$$\frac{A_{centre}}{A_{SiO_2}} = \frac{A_{MoSi} + A_{walls} + A_{clear}}{A_{SiO_2}} \quad (1)$$

where we consider that the contributors to the centre of the (structured) mask area are: MoSi features, their side walls and clears (i.e. quartz after MoSi etch) then one can easily conclude that the retention rate is not area determined, but correlates well with the substrate type. Taking Eq. 1 into account the following relation of the ions concentration can be obtained:

$$\begin{aligned} [SO_4^{2-}]_{SiO_2} &> [SO_4^{2-}]_{MoSi} \\ [NH_4^+]_{SiO_2} &< [NH_4^+]_{MoSi} \end{aligned} \quad (2)$$

A separate discussion must be dedicated to the presence of molybdates. Akutsu et al. [1] mentioned the presence of molybdates on hazed MoSi masks too. In their article they propose several haze formation mechanisms leading to end products involving molybdates. While this is a relatively new subject we would like to address it in more details.

4.3 Formation mechanisms

We start our reasoning from two premises: (i) masks are clean (or at least contaminants from mask manufacturing are not enough to build large defects) and (ii) the only sources of contaminants are mask substrate itself and environment (storage, pellicle, etc.). Independent on the contaminants source the total amount of reactants is generally low and it should exist an efficient surface migration mechanism which facilitates the formation of defects of detectable size. This is possible only in the presence of a water film on the mask which is turn is possible in humid environments. The water presence is mirrored in the morphology of the haze products too: they are destroyed during illumination, i.e. their nature can be but aqueous.

Figure 8 depicts what we think the haze formation path is. We distinguish 2 main phases: early and advanced stage of haze growth. Kishkovich et al. [2] proposes that SiO_2 is transformed into silicic acid upon cleaning during mask manufacturing. In the early stage the formed silicic acid plays a crucial role in attracting and trapping ammonium and sulphates from the atmosphere. Enhanced by humidity the surface migration of these contaminants is easily possible which leads to their consumption in reactions leading to formation of ammonium sulphates.

In its early stage haze will form on quartz and features side walls including migration to the features top. Vigorous illumination will however efficiently destroy the haze defects on quartz. Additionally the defects on the features side will be also attacked. However, while the electric field components are all zero at metallic interfaces and hence the electromagnetic (EM) field intensity is low at the side walls, at the sharp corners the EM intensity increases drastically [6] (page 553 - 587). This is the reason why such a periodic distribution of the defects can be seen: haze always present on the features side and on the features top short before their edge.

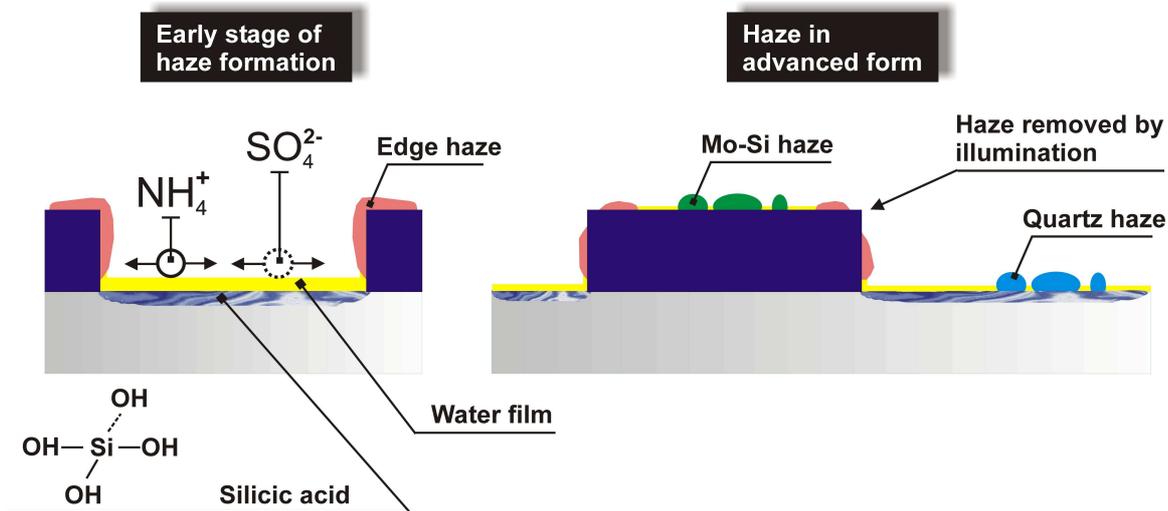


Figure 8 Stages of haze formation. In the early stage quartz is affected as well as sides of the features. Illumination plays a crucial role in re-arranging the defects on the mask. (Layers, structures and ions are not at true scale; only schematic representation to guide the reader!)

The migration of the contaminants from quartz is not able to explain the haze growth on MoSi, however. We think different mechanisms should be invoked. In what follow the haze formation on MoSi will be discussed from the perspective of the presence of molybdates.

We consider the possibility that MoSi thin films are an important source of ammonium. In general the presence of ammonium on the film surface will stabilize the formation of molybdates, e.g. MoO_4^{2-} , $\text{Mo}_7\text{O}_{24}^{6-}$ [7]. In our measurements we could detect up to 9 times higher concentration of MoO_4^{2-} on a hazed mask compared to a mask without haze. The role of molybdates can be viewed as follows: (i) they come from the oxidized MoSi features or (ii) are part of the haze defects. We analyze these possibilities in more details.

4.3.1 Molybdates: features oxidation only

An exact form of the oxide found on MoSi structures could not be identified (always too small) [5]. It was generically named as MoSiON [4] which in any case will deliver a strong signal for molybdates if analyzed with Ion Chromatography. Since oxidation was related to the depletion of nitrogen which in turn leads to the formation of ammonium on MoSi surface obviously the haze defects will be mainly ammonium sulphates with high water content. In this case there is no difference between what is formed as haze on quartz or features side wall and edge haze.

4.3.2 Molybdates: part of the haze defects

In this case two possible mechanisms can be invoked: clustering of protonated (or not) molybdates or the formation of ammonia molybdates salts. The general equation of molybdates clustering is shown in Eq. 1. One can see that an acidic environment is required. In Eq. 1 p - amount of protons, q - amount of molybdate monomers. The number r indicates how many molybdates stick into a cluster. For the case when non protonated molybdates have to be treated $r = p/2$



The literature reports that clusters of $q=7$ ($(p,q)=(8,7), (9,7), (10,7)$ or $(11,7)$) and $q=8$ ($(p,q)=(12,8), (13,8)$) exist and are thermodynamically stable [8]. Clusters can be also built if $q=12$, $q=18$ or $q=36$. The (local) acidic environment is expected to be caused by the formation of H_2SO_4 during the mask illumination [9].

Alternatively the molybdates, as charged ions, can undergo ionic bonds with available ammonium. In this case we expect that a salt similar in structure to $n\text{H}_2\text{O} \cdot (\text{NH}_4)_2\text{MoO}_4$. Certainly this represents only a possible product in which case Molybdenum (VI) is involved. However, there are plenty of other molybdates types which could undergo the formation of such salts [10]. Again water (and hence humidity) is involved.

The exact role of illumination in the haze formation mechanism (not its distribution) remains unclear. Suffices to mention that haze could not be found on extremely large MoSi layers or on features side walls or on quartz in non illuminated areas. At least to what haze formation on MoSi is concerned, due to partial (or complete) absorption of light in MoSi the heating of the absorber might play a role. The Tamman temperature of molybdenum oxides was reported to be around 250°C [11] at which enhanced migration mechanisms on MoSiON surface would be expected. However clear data about the temperature a mask reaches during the illumination are missing.

5. CONCLUSIONS

In our article we have analyzed a very enticing form of haze formation which takes place under “extremely” clean conditions: low ionic contamination on the mask and in the environment. Due to extremely small sizes it was difficult to obtain a detailed material analysis of the haze defects. This leaves a plethora of open questions with respect to haze formation. Particularly the role of the detected molybdates is not really clear, but it can be speculated that they are either an indication of early stage of classical haze formation or represent a new type of haze: clusters or salts.

Similarly to other authors we could confirm that water plays a crucial role: it is decisive in any surface diffusion mechanisms which proved to be essential for haze formation, but it also participates in any kind of haze products treated

in this paper. The role of illumination in the haze formation mechanism was not analyzed. It might contribute to the substrate heating and hence migration mechanism related herewith.

Finally we tried to show that the race for reducing sulphates and ammonium on the mask surface might be contra productive. As Nesladek et al. showed there exist numerous methods for contaminants reduction on the mask surface [...]. Each of these methods would work at the expense of strong mask surface modifications. Although showing low contaminants level on the masks while leaving the mask shop, their surface might be brought in such a state that later during the mask use the formation of haze is strongly promoted with airborne contaminants or supplied by the stack. The surface condition and material plays a crucial role in formation of small defects which are meanwhile easily detected by advanced inspection tools. In this particular case the amount of sulphates and ammonium might be of not such a big importance, but rather the condition of the mask surface at the delivery from the mask shop.

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