Effects of chromium on the reactive ion etching of steep-walled trenches in silicon

N. I. Maluf, S. Y. Chou, J. P. McVittie, S. W. J. Kuan,[a] D. R. Allee, and R. F. W. Pease
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

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Formation of vertical-walled, high-aspect-ratio, narrow trenches in silicon is often required in submicron VLSI semiconductor processing. Present trench etching processes suffer from undercutting of the mask and sloped or bulged sidewalls; and when using chlorine-based reactive ion etching (RIE), there is frequently enhanced etching at the bottom corners of the trench. We report here the effects of chromium on the RIE of silicon. We found that, compared to using a SiO_2 mask only, using a mask consisting of a chromium layer on top of SiO_2, in a Cl_2:$SiCl_4$:N_2 etching gas mixture, improves the trench sidewall angle relative to the vertical from 8° to 2°, and almost eliminates the enhanced etching at the bottom corners. Furthermore, we found that, by etching a sample partially covered with chromium in a Cl_2:$SiCl_4$:N_2 gas mixture, the trench shape in the areas not covered with chromium depends on how far the trench is from the edge of the chromium layer. Those areas, within 1 cm of the edge of the chromium layer, showed quite steep sidewall angles that degraded (to 8°) at greater distances (few cm). Similarly, the size of the grooves due to the enhanced etching at the bottom corners is reduced as the trench gets closer to the edge of the chromium layer. It appears that the beneficial effect of the chromium is an indirect chemical action, based on the suppression of the concentration of neutrals or the formation of an inhibitor layer, rather than direct physical masking.

I. INTRODUCTION

Reactive ion etching (RIE) of silicon has become a key processing step in submicron VLSI technology, such as in the fabrication of trench capacitors,[1] trench isolation,[2] power devices,[3,4] or x-ray masks that employ the embedded absorber structure.[5] Even though present trench etching processes have been used to fabricate sub-100 nm trenches,[6,7] they often suffer from undercutting of the mask and sloped or bulged sidewalls. Furthermore, the profiles of trenches etched in processes using chlorine based chemistries exhibit enhanced etching at the bottom corners of the trenches.[8,9] These problems result in many undesirable effects such as increased leakage current or lowered breakdown voltage in trench capacitors, or severe linewidth control in x-ray lithography. Moreover, the enhanced etching at the bottom corners poses a serious technological challenge as to preventing void formation in the filling of the trenches. This paper presents the effects of using a masking chromium layer on the trench profiles formed in silicon by RIE.

II. EXPERIMENTS

In all the experiments, a Zylin etcher, model ZLN20, operating in the RIE mode was utilized to etch the trenches in silicon. The starting wafers were 4 in. in diameter, *n*-type and had a resistivity of 5 Ω cm with (100) orientation. Initially, a 100 nm thick layer of SiO_2 was thermally grown. A thin (50 nm) layer of chromium was then evaporated on some of the *n*-type wafers. The remaining wafers were used as control wafers for comparison. For submicron line definition, the patterning was done using either a Perkin–Elmer MEBES-I system or a custom built high resolution electron beam tool[10] writing on ultrathin (15 nm) poly(methylmethacrylate) (PMMA) deposited by Langmuir–Blodgett technique to minimize electron scattering. The details of the deposition and characterization of the PMMA are discussed elsewhere.[11] For wider line definition, positive photoresist was patterned using conventional optical lithography. The chromium was then chemically etched in a CR-14 Cyantek solution for 30 s. The SiO_2 was reactive ion etched in a CHF_3/O_2 plasma with a selectivity of more than 50:1 to chromium, and more than 10:1 to positive photoresist. The photoresist or the PMMA were stripped before the trench formation.

The RIE of the silicon was mainly performed in two different gas mixtures, Cl_2:$SiCl_4$:N_2 and Cl_2:$SiCl_4$:He. The etching gas pressure and self-bias voltage were 40 mTorr and − 500 V, respectively, and the rf power density at 13.56 MHz was 2W/cm^2. The cathode was kept at 40 °C during the etching process. The etching conditions are summarized in Table I. The sheath thickness was measured for both discharges using a microscope micrometer, and was found to be 1 cm. In contrast, the mean free path of the ions in the sheath was estimated to be 0.25 cm, indicating that these ions will suffer collisions.

Another experiment was performed where two samples,

TABLE I. Summary of etching conditions.

	Cl_2:$SiCl_4$:N_2	Cl_2:$SiCl_4$:He	Cl_2
Cl_2 flow	85 sccm	85 sccm	85 sccm
$SiCl_4$ flow	15 sccm	15 sccm	...
N_2/He flow	29 sccm	40 sccm	...
Si etch rates with Cr	90 nm/min	180 nm/min	90 nm/min
Si etch rates without Cr	150 nm/min	180 nm/min	150 nm/min
Chromium etch rate	17 nm/min	17 nm/min	17 nm/min
SiO_2 etch rate	17 nm/min	17 nm/min	17 nm/min
rf power	2 W/cm^2	2 W/cm^2	2 W/cm^2
pressure	40 mTorr	40 mTorr	40 mTorr
self bias	− 500 V	− 500 V	− 400 V

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with and without the chromium layer, were etched using only Cl_2 gas. The etch conditions remained the same as in the previous experiments with the exception that the dc bias dropped to -400 V when the incident power was maintained at 2W/cm^2. The sheath thickness was again measured to be 1 cm.

III. RESULTS

A. Etch rates

The etch rates of SiO_2 were determined using either an ellipsometer (Guertner Scientific Corporation) or a Nanospec (Nanometrics/AFT). The silicon and chromium etch rates were determined by measuring the trench depths using a Dektak stylus and by examining the trenches using scanning electron microscopy.

In the case of masking with a chromium layer, the etch rate of silicon was found to be 90 nm/min in a Cl_2:$SiCl_4$:N_2 gas mixture, and about 180 nm/min in a Cl_2:$SiCl_4$:He gas mixture. The etch rate of silicon on the control wafers were 150 nm/min in a Cl_2:$SiCl_4$:N_2 gas mixture, and about 180 nm/min in a Cl_2:$SiCl_4$:He gas mixture. The etch rate of the SiO_2 and of the chromium in either gas mixture, were both approximately 17 nm/min.

In the experiment where only Cl_2 was used as the etching gas, the etch rates and trench profiles were found to be identical to those obtained using the Cl_2:$SiCl_4$:N_2 gas mixture despite the drop in the dc self-bias.

B. Etching in a Cl_2:$SiCl_4$:N_2 gas mixture or Cl_2

The early experiments were performed without using the chromium layer and resulted in a sidewall angle relative to the vertical of approximately 8°, and in the enhanced etching of the corners at the bottom of the trenches [Fig. 1(a)]. The mechanisms that influence the shaping of the trench are numerous, and many of them still remain unclear; however, we suspected that the erosion of the edges of the SiO_2 mask during the etching, due to the selectivity (9:1) between SiO_2 and Si, would degrade the sidewall angle. Initially, we chose the chromium as an additional masking layer due to its ruggedness. However, we found that the etch rate of silicon was reduced by almost a factor of 2 and that the sidewall angle was reduced to about 2°. Furthermore, the enhanced etching at the bottom corners seems to have been eliminated. These effects are illustrated in Fig. 1(b) which shows 1 μm wide trenches in silicon, 500 nm deep. The bottom of the trenches show no enhanced etching and the sidewalls show an improved sidewall steepness. Using the above process, trenches 70 nm wide, 500 nm deep, resulting in an aspect ratio of 7:1, were fabricated.[5]

The combination of the raggedness in the lines due to e-beam or optical lithography, along with the initial chemical etching of the chromium layer, resulted in nonuniform edges. This edge nonuniformity was transferred during the dry etching processes to the underlying SiO_2 layer and subsequently to the silicon resulting in the formation of non-smooth sidewalls [Figs. 1(a) and 1(b)].

To verify that the chromium is responsible for the improved sidewall angles and flat bottoms, the etch time was extended beyond the 3 min necessary to completely etch the 50 nm chromium layer. As shown in Fig. 2, a bowing of the sidewalls is observed due to a change in the angle at a depth of approximately 270 nm. This is attributed to an initial steep angle resulting from the presence of the chromium layer; but as soon as the chromium is etched away, the slope is degraded and the sidewalls at the bottom of the trench form a larger

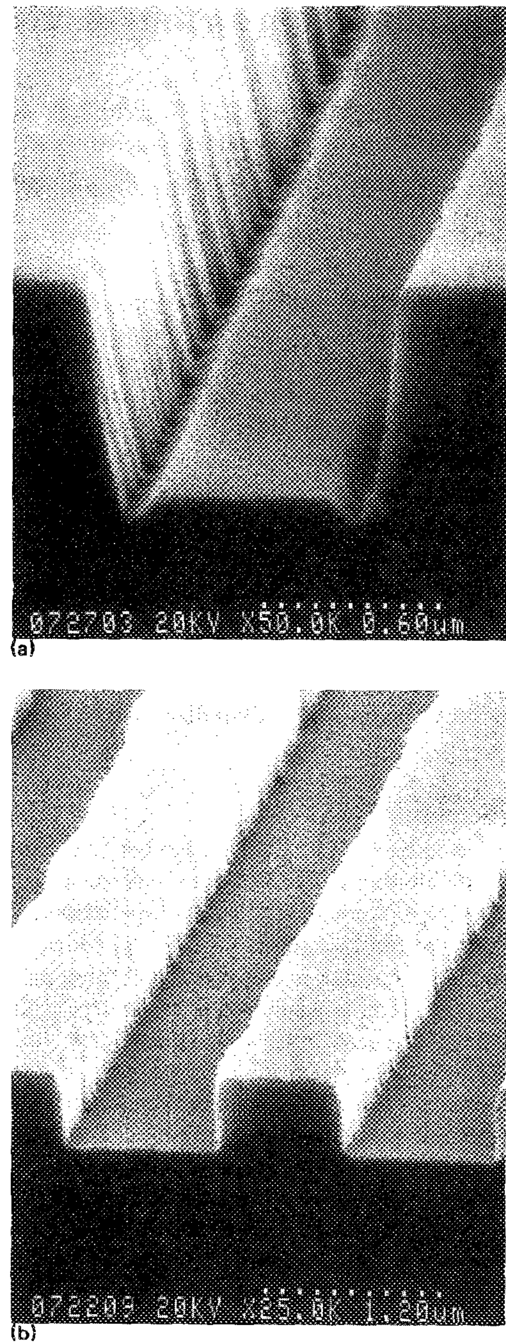
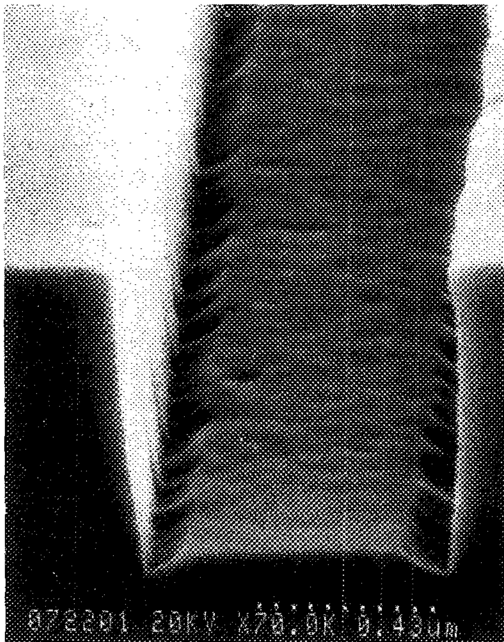


FIG. 1. (a) Current etching processes that use chlorine-based chemistries often suffer from sloped widewalls and enhanced etching at the bottom corners of the trench. This figure shows a 1 μm wide trench, that was masked with a 100 nm thick SiO_2 mask, and etched in a Cl_2:$SiCl_4$:N_2 gas mixture to a depth of 500 nm. The sidewall angle with the vertical is 8° and grooves have formed at the bottom corners due to the local enhanced etching. (b) When using a mask consisting of a 50 nm thick chromium layer on top of SiO_2 in a Cl_2:$SiCl_4$:N_2 gas mixture, we observed an improvement in the sidewall angle from 8° to 2°. Moreover, the enhanced etching at the bottom corners of the trenches is eliminated.



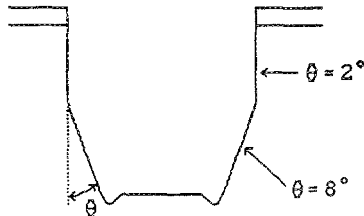


FIG. 2. To double check that the chromium is responsible for improving the sidewall angle and eliminating the enhanced etching at the corners, a trench was etched in a Cl_2:$SiCl_4$:N_2 gas mixture for 5 min, 2 min longer than the time necessary to completely etch away the chromium layer. The trench sidewall became bowed indicating a change in the angle at a depth of 270 nm, at which the chromium layer was totally etched. Furthermore, enhanced etching at the bottom corners was observed, therefore verifying that chromium eliminates this phenomenon.

angle with the vertical. In addition, enhanced etching at the bottom corners of the trenches is observed after the chromium is completely etched away, confirming that the presence of the chromium eliminates this phenomenon.

Nonlocal effects were investigated by partially covering few samples with chromium, and etching the trenches in a Cl_2:$SiCl_4$:N_2 gas mixture. It was found that the sidewall angle of the trenches in the uncovered regions, but within 1 cm from the edge of the chromium layer, remained quite steep (Fig. 3); the angle degraded to approximately 8° at a distance of a few cms. Moreover, the size of the grooves formed by the enhanced etching at the corners, was reduced as the separation between the trench and the edge of the chromium layer became smaller.

It also appears that the trench profile is independent of heavy boron doping. Trenches were etched using the same conditions in a heavily boron doped wafer, with a surface concentration of $\sim 3\times 10^{20}$ cm^{-3} formed by predeposition in a BBr_3 source at 1100 °C for 3 h. The trench shapes were similar to the ones etched in the n-type wafers.

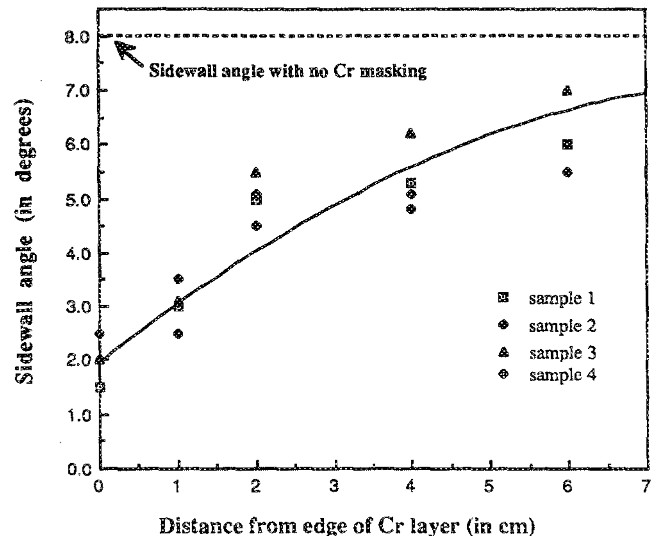


FIG. 3. A sample was partially covered with chromium and etched in a Cl_2:$SiCl_4$:N_2 gas mixture. It was observed that the sidewall angle within 1 cm from the edge of the chromium layer remained steep, but degraded to 8° over few cms. This finding indicates that the chromium effect is an indirect chemical action rather than physical masking.

C. Etching in a Cl_2:$SiCl_4$:He gas mixture

Figure 4(a) shows a trench in a sample etched in a Cl_2:$SiCl_4$:He gas mixture without the masking chromium layer. There is clear enhanced etching at the bottom corners of the trench, however, unlike etching in a Cl_2:$SiCl_4$:N_2 gas mixture, the sidewall angle is steep ($\sim 3°$). Figure 4(b) shows a trench etched in the sample with the chromium layer. The enhanced etching has been greatly reduced but both the etch rate and the sidewall angle seem to be unchanged.

When the flow of the He gas was increased to over 60 sccm, the formation of rough surfaces (black silicon) was observed in the etched regions.

The etch rates and trench profiles also appear to be independent of the heavy boron doping (surface concentration of $\sim 3\times 10^{20}$ cm^{-3}).

IV. DISCUSSION

The fact that the effects of the masking chromium layer are nonlocal, and extend over a distance of a few cms, is an important finding. Its significance lies in determining that these effects are related to an indirect chemical action, rather than direct physical masking. In addition to the nonlocal effects, three other findings need to be addressed: (1) the improvement in the sidewall angle when using either Cl_2 gas or a Cl_2:$SiCl_4$:N_2 gas mixture; (2) the elimination of enhanced etching at the bottom corners; and (3) the sharp reduction in the etch rate. This leads us to examining the mechanisms of etching silicon and the dominant chemical reactions in plasma and RIE.

These mechanisms have been studied in previous works and models have been proposed to explain various aspects of the etching process such as the occurring surface reactions,[13–18] and the enhanced etching at the bottom corners[8]

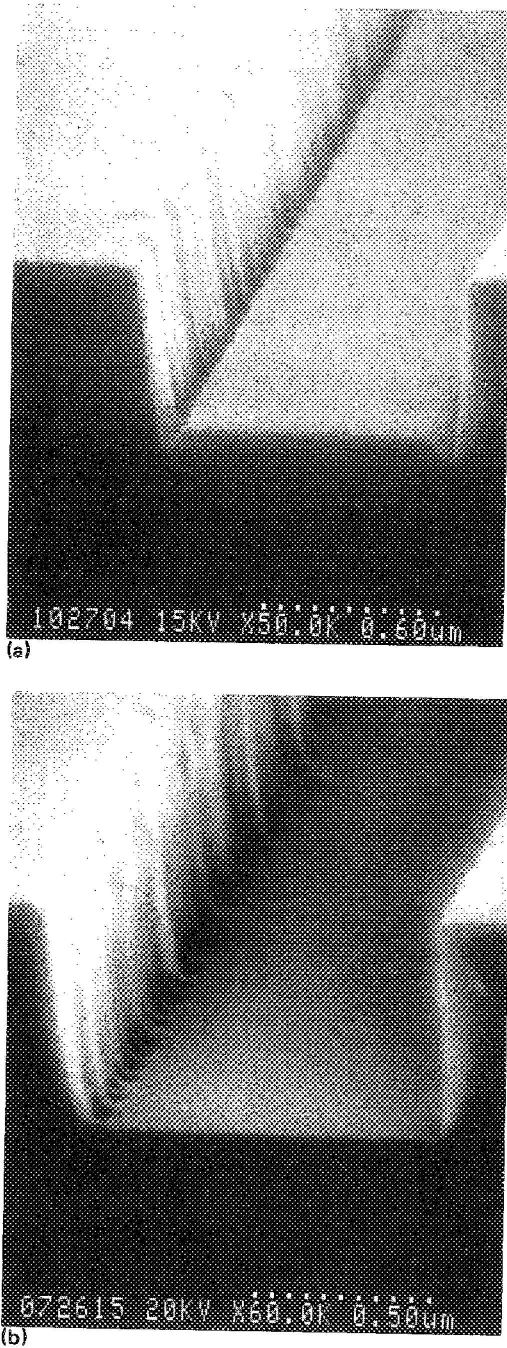


FIG. 4. (a) Changing the etching gas mixture to Cl_2:$SiCl_4$:He results in a higher etch rate and improved sidewall angle. However, the enhanced etching at the corners does not disappear, a characteristic of chlorine based chemistries. (b) The enhanced etching at the corners, observed in (a) is greatly reduced by using a chromium layer on SiO_2. The sidewall angle remains steep.

that often exists in chlorine based chemistries. It is believed that the etching is achieved by the ions (such as Cl^+) and neutrals (such as Cl_2 and Cl) chemically reacting with silicon, and by the incident ions also promoting a reaction between the neutrals that have adsorbed onto the surface and the silicon atoms.[16,17] The latter reaction, commonly referred to as ion assisted etching,[14] is generally attributed to momentum transfer between the incoming ions and the surface atoms and is believed to be the dominant etching process.[17,18]

Since the sheath thickness was found to be larger than the ion mean free path, the ions will suffer collisions resulting in the broadening of the angular distribution of the ions and their energies[19]. Therefore, there will be a flux of ions reaching the sidewall surfaces and initiating a reaction between the adsorbed neutrals and the silicon atoms. The resulting etching will cause an increase in the sidewall angle (as measured to the vertical).

The findings that the sheath thicknesses, when etching in Cl_2 gas or Cl_2:$SiCl_4$:N_2 or Cl_2:$SiCl_4$:He gas mixtures, are equal, and that the self-biases, when using the latter two gas compositions, are also similar, suggest that the chlorinated species are dominating in all three discharges.

A. Improvement of sidewall angle

In general, we can represent the total etch rate R of either the bottom or sidewall surfaces as the sum of the individual contributions of the etch rate due to the incoming ions R_{ion} and the etch rate due to the neutrals spontaneously reacting with the Si, R_{nr}, and the etch rate due to the reaction of the adsorbed neutrals promoted by the incident ions R_{prom}:

$$R = R_{\text{ion}} + R_{nr} + R_{\text{prom}}.$$

At the bottom surface of the trench, R_{ion} is a function of the flux of incident ions, $\Phi_{\text{ion}}^{\text{bottom}}$, reaching that surface, R_{nr} is a function of the concentration of neutrals, $[NR]$, and R_{prom} is a function of both $[NR]$ and of the flux $\Phi_{\text{ion}}^{\text{bottom}}$. At the sidewalls, R_{ion} depends on the flux of ions $\Phi_{\text{ion}}^{\text{sidewalls}}$ reaching the sidewall surfaces; R_{nr} then depends on $[NR]$, and R_{prom} depends on $[NR]$ and $\Phi_{\text{ion}}^{\text{sidewalls}}$. The improvement of the sidewall angle by using chromium can be attributed to a further reduction in the total lateral etch rate R of the sidewalls; such a reduction would be related to either (i) a reduction in $\Phi_{\text{ion}}^{\text{sidewalls}}$ or (ii) the formation of an inhibitor layer or (iii) a reduction in $[NR]$ or a combination thereof. A reduction in $\Phi_{\text{ion}}^{\text{sidewalls}}$ is unlikely because it would result in a change in the sheath voltage and thickness. The formation of an inhibitor layer on the sidewall surfaces brings about improved anisotropy, and its formation on the bottom surface may cause a decrease in the total etch rate at the bottom surface. Similarly, a reduction in $[NR]$ would result in the decrease of the etch rates at the sidewalls and the bottom surface.

B. Elimination of the enhanced etching at the bottom corners

The enhanced etching at the bottom corners is generally the result of (i) stress at the corners, or (ii) excess etching species. However, since stress is a local effect and masking with chromium was shown to have a nonlocal action (Fig. 3), we conclude that this phenomenon is not related to stress.

The increase in the etching species concentration at the corners is brought about by either the reflection of the incoming ions off the sidewalls or the diffusion or migration of the neutrals to these corners.[8,17]

When an ion hits a sidewall surface, elastic scattering is the dominant process because inelastic scattering will most likely result in the generation of a single phonon whose ener-

gy is much smaller that the incident ion's energy. Incoming ions at an angle with the vertical, would have similar energies and therefore would all be reflected along a similar direction because of the little or no loss of energy suffered upon their collision with the silicon atoms. Hence, if the enhanced etching were due to ion reflection, the shape and the location of the groove would depend on the sidewall angle. However, no such dependence was observed when etching in Cl_2:$SiCl_4$:N_2 and Cl_2:$SiCl_4$:He gas mixtures which yielded sidewall angles of 8° and 3°, respectively, hence indicating that ion reflection is not responsible for the enhanced etching at the bottom corners of the trenches.

A model has been presented[8] where the neutrals are assumed to be mobile. These species may migrate down the surface of the sidewalls to the corners where their reaction with the silicon is greatly enhanced due to the higher flux of incident ions at the bottom surface. The increased local concentration of the neutrals results in the enhanced etching. The effect of masking with a chromium layer may be attributed to either a reduction of the neutrals thereby suppressing the enhanced etching of the corners, or a decrease in the mobility of the neutrals by modifying the nature of the sidewall surface, such as the formation of an inhibitor layer.

V. SUMMARY

It was found that using chromium as a masking layer improves the sidewall angle of trenches in silicon etched in a Cl_2:$SiCl_4$:N_2 gas mixture. Furthermore, it was found that it eliminates enhanced etching at the bottom corners when either a Cl_2:$SiCl_4$:N_2 or Cl_2:$SiCl_4$:He gas mixture is used. Both effects also were observed in regions unmasked with chromium but within a few cms from the edge of a chromium layer masking an adjacent region.

Preliminary experiments indicate that these effects may be brought by the reduction of the neutrals or by the formation of an inhibitor layer.

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