High-Temperature SiO_2 Decomposition at the SiO_2/Si Interface

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The high-temperature decomposition of thin (~ 100 Å) SiO_2 layers on Si(001) under ultrahigh-vacuum annealing conditions has been studied by means of ion scattering and microscopy techniques. SiO_2 is removed from the Si surface by the formation and lateral growth of holes in the oxide, exposing regions of atomically clean Si, while the surrounding oxide retains its initial thickness. Surface diffusion of Si inside the holes supplies Si for reaction with SiO_2 at the periphery, so that a volatile product (presumably SiO) can be formed.

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The formation of thin SiO_2 layers on Si surfaces by high-temperature (~ 900–$1100\,°C$) oxidation can yield very uniform oxides and Si/SiO_2 interfaces which have extremely high electrical quality and form the basis for Si field-effect-transistor (FET) technology.[1] Even though many studies of Si oxidation and Si/SiO_2 interface properties have been carried out, the fundamental steps involved in the oxidation process are still not fully known at a microscopic level.

At the same temperatures but under high vacuum conditions (i.e., in the absence of O_2), thin oxide layers on Si undergo reaction which decomposes the SiO_2. This process results in complete removal of the oxide from the Si surface[2] and is exploited in surface science for studies of high-quality, atomically clean Si surfaces. It appears likely that this decomposition process may play a role in the properties of thermally grown SiO_2 layers on Si upon subsequent annealing not only in vacuum[3] but also in O_2-free gaseous ambients[4] as is crucial in FET technology. In spite of its scientific and technological significance, very little (if any) attention has been given to understanding this SiO_2 decomposition process.

We have studied changes in dry thermal SiO_2 layers on Si(001) upon high-temperature annealing in ultrahigh vacuum (UHV), using *in situ* high-resolution ion scattering followed by scanning electron microscopy (SEM), scanning Auger microscopy (SAM), and cross-sectional transmission electron microscopy (TEM). These results reveal for the first time the mechanisms by which SiO_2 decomposition occurs and the oxide is removed from the Si substrate. In contrast to the lateral uniformity of the Si oxidation process, the SiO_2 decomposition process is highly nonuniform: Holes are formed in the SiO_2 layer, exposing regions of atomically clean Si, while the surrounding oxide retains its initial thickness. Surface self-diffusion of Si inside the holes supplies Si for reaction with SiO_2 at the periphery of the holes, where a volatile product (presumably SiO) can be formed, causing the holes to increase in size. Even though the decomposition process affects only a small fraction of the total oxide at normal annealing temperatures (~ 900–$1050\,°C$), this process may have considerable technological significance: Its high degree of nonuniformity leads to defect generation in a system where extremely low defect densities are required for application in metal-oxide-semiconductor field-effect-transistor technology.

Dry thermal SiO_2 layers of device quality were grown at 900 °C to thicknesses of 50, 100, and 300 Å on Si(100) substrates, followed by cooling in dry nitrogen. The wafers were then cut to samples of size $\simeq 7\times 15$ mm^2. Annealing treatments up to 1150 °C were carried out in ultrahigh vacuum (8×10^{-11} Torr during annealing) by use of direct resistive heating of the samples in the high-resolution medium-energy ion-scattering facility at the Fundamental Research of Matter (FOM) Institute in Amsterdam. *In situ* ion-scattering measurements were carried out before and after different annealing steps. New spots on the sample were used for each measurement to ensure that the ion beam did not influence the high-temperature reaction process. After completion of the annealing treatments and ion-scattering studies, the samples were removed from the UHV chamber and further analyzed with cross-sectional TEM as well as SEM and SAM. For cross-sectional TEM studies a Cr overlayer ~ 300 Å thick was deposited to provide contrast with the surface topography of the sample.

Ion-scattering spectra for a 100-Å SiO_2 layer on Si(001) are shown in Fig. 1 for a sequence of annealing steps as indicated. These spectra were obtained with a 120-keV He^+-ion beam incident along the $[11\bar{1}]$ direction of the Si(001) substrate and detected along the [111] scattering direction, at a scattering angle of 70.5°. Spectrum *a* was obtained before the crys-

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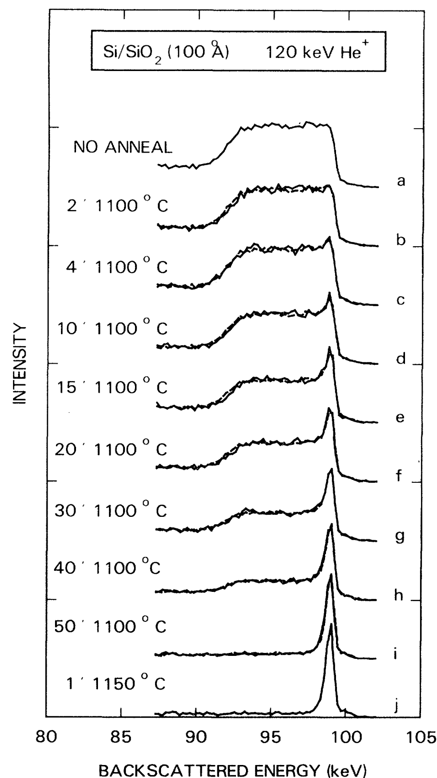

FIG. 1. Ion-scattering spectra for a range of ultrahigh-vacuum annealing treatments (with total annealing times indicated in minutes), including the as-prepared (unannealed) sample (curve *a*), intermediate annealing steps (curves *b*–*i*), and the clean Si substrate surface after complete removal of the SiO_2 layer (curve *j*). The width of the as-prepared SiO_2 spectrum represents the depth distribution of Si concentration in the SiO_2 layer, with the SiO_2 top surface and the Si/SiO_2 interface at high- and low-energy edges, respectively.

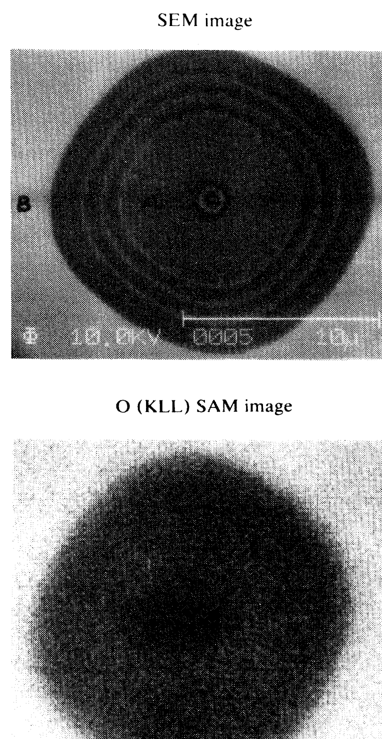

FIG. 2. SEM and SAM O(*KLL*) micrographs for ultrahigh-vacuum annealing of a 300-Å-SiO_2 layer on Si(001) until about 15% of the surface is oxide free.

tal was subjected to any annealing. The broad peak between ~92 and 99 keV is due to backscattering of ions by Si atoms in the SiO_2 film and atoms in the underlying substrate close to the Si/SiO_2 interface. Atoms deeper in the crystal do not give rise to backscattering because of the channeling effect, which causes a reduction of backscattered yield at lower energies. The width of the peak is proportional to the thickness of the SiO_2 layer. From the sharpness of the low-energy side of the peak we see that the oxide is very uniform in thickness. Spectrum *j* was measured after the SiO_2 layer had been completely removed by high-temperature annealing. In this case backscattering occurs only close to the atomically clean surface of the Si(001) crystal. Spectra *b* through *i* were obtained after intermediate stages of annealing as indicated.

Two striking observations are evident in the ion-scattering spectra. First, the spectra at intermediate stages of annealing all appear as a superposition of the SiO_2 spectrum [Fig. 1 (curve *a*)] and the clean Si spectrum [Fig. 1 (curve *j*)]. In fact, all intermediate spectra have been successfully replicated by such a model in which the entire surface consists only of clean Si surface regions and SiO_2-covered regions with the initial SiO_2 thickness, as shown by the dashed lines in Fig. 1. Second, the width of the SiO_2 distribution does not change with annealing, demonstrating that the SiO_2 thickness of oxide-covered surface regions on Si(001) does not change during the SiO_2 decomposition and removal process.

These results demonstrate clearly that the decomposition and removal of the SiO_2 layer does not proceed through a gradual and uniform decrease in thickness of the oxide. Instead, the SiO_2 is removed from some portions of the surface while the remaining portions are unaffected. This was also confirmed by the observation of a (2×1) LEED pattern [which is characteristic of the atomically clean Si(001) surface] when the SiO_2 had been only partially removed; the diffraction pattern also showed a high elastic background caused by the remaining SiO_2.

The morphology of the oxide-free regions of the surface at an intermediate stage of the decomposition and removal process (about 15% of the surface free of oxide) is depicted in the SEM and SAM (oxygen

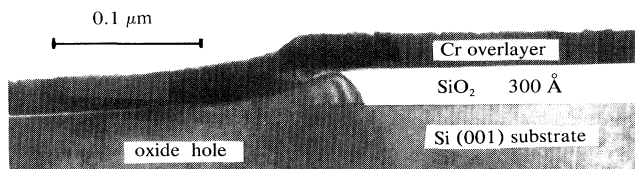

FIG. 2. Cross-sectional TEM micrograph for ultrahigh-vacuum annealing of a 300-Å-SiO_2 layer on Si(001) until about 15% of the surface is oxide free. Before preparation of the sample for cross-sectional TEM analysis, it was covered with ~300 Å of Cr to provide a contrasting layer between the SiO_2 and the glue used in the sample preparation.

KLL) images in Fig. 2 for a similar SiO_2 film 300 Å thick. Nearly circular regions of order 10 μm in diameter have been formed, with a slight fourfold noncircular shape corresponding to the symmetry of the (001) surface. Since the O(*KLL*) SAM image is brighter outside the circular region, we conclude that oxide is present only outside the region, with clean Si inside. Thus the oxide-free regions of the surface consist of "holes" in the oxide layer,[5] of order 10 μm in diameter at this stage of oxide removal. Many such holes are readily observed across the surface. Correlation between the rings evident inside the hole seen in the SEM image and the number of heating and cooling cycles used in the sequential annealing process suggests that the rings are associated with irregularities in surface morphology generated by these cycles.

A cross-sectional TEM image of the sidewall of a hole in the oxide is depicted in Fig. 3 for a similar sample with 300-Å oxide thickness. This image reveals a number of important characteristics.

First, the remaining Si/SiO_2 interface outside the hole is sharp, as is the SiO_2 surface (interface with the Cr overlayer); this characteristic confirms the integrity of the oxide remaining outside the holes.

Second, the oxide sidewall is undercut, suggesting that SiO_2 decomposition and removal which has caused the growth of the hole has occurred faster near the Si/SiO_2 interface. This suggests that the reaction responsible for SiO_2 removal is $Si + SiO_2 \rightarrow 2SiO$, where SiO is a volatile desorption product at these high temperatures. Its equilibrium pressure has a considerable value (e.g., 10^{-4} bar at 1200 °C) for O_2-free conditions.[6]

Third, the Si substrate surface inside the hole lies below the Si/SiO_2 interface plane, especially nearer the center of the hole. This suggests that Si has traveled to the SiO_2 sidewall (where reaction occurs) by surface diffusion from the entire region of the hole.[7]

Finally, extra Si is present at the periphery of the holes, appearing in the shape of a meniscus against the sidewall. This Si is observed above the original Si/SiO_2 interface, which appears as a line extending from the Si/SiO_2 interface at the right. (This line appears because we look at the oxide wall in projection through a sample of finite thickness; this is also evident from the thickness fringes observed in the meniscus area.) It seems likely that during cooling after the high-temperature annealing step the Si surface diffusion continues while the Si-SiO_2 reaction stops, resulting in an excess of Si at the sidewall. The meniscus shape of the Si surface near the oxide wall confirms the extremely fast surface self-diffusion of Si, allowing it to behave as if it were a liquid. This process may also be responsible for the rings evident in Fig. 2(a) at positions correlated with the heating and cooling cycles of the annealing sequence used. Cross-sectional TEM does not indicate significant protrusions from the Si surface where the oxide has been removed.

These results provide a first microscopic picture of the high-temperature decomposition reaction which occurs for SiO_2 on Si surfaces. Although the steps involved in initiating the reaction are not yet known, they would seem to include nucleation of holes at defects in the oxide or at the interface. Once the holes are formed, Si is supplied by surface self-diffusion across the clean Si surface inside the hole, and reaction of this Si with the SiO_2 proceeds at the edges of the hole, particularly near the interface; both the depression in the Si surface in the hole and the undercut of the SiO_2 sidewall support this picture. This is consistent with the reaction $Si + SiO_2 \rightarrow 2SiO$(volatile), as suggested by previous studies, but for the first time the microscopic position (at the interface and along the SiO_2 sidewall) where it occurs has been revealed.

The prominent lateral inhomogeneity associated with the reaction suggests that defects play an important role in the decomposition. Such defects might be spontaneously generated in the oxide or at the Si/SiO_2 interface during high-temperature annealing; alternatively, they might already be present after oxidation, either as intrinsic defects like micropores[8,9] or as extrinsic defects like metal impurities. In any case, the SiO_2 decomposition reaction may have significant technological implications because of the high temperatures used in oxidation and post-annealing of Si FET devices.

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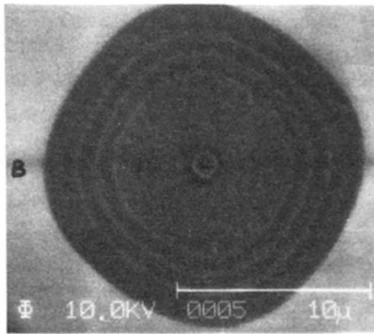
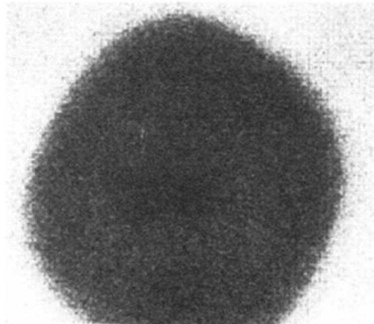
SEM image



O (KLL) SAM image



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