Kinetics of high-temperature thermal decomposition of SiO$_2$ on Si(100)

M. Liehr, J. E. Lewis, and G. W. Rubloff

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 22 September 1986; accepted 1 December 1986)

The decomposition of oxide films of 50 to 500 Å on Si(100) during ultrahigh vacuum anneal has been studied in a scanning Auger microscope. The decomposition of the oxide occurs locally, in that voids form in the oxide and grow laterally with time and temperature, leaving the oxide areas in between unperturbed. Void growth kinetics data are derived from in situ absorbed current and secondary electron imaging during vacuum anneal. The growth of the void diameter is found to be linear in time with an activation energy of 2.0 ± 0.25 eV. This implies that oxide decomposition rates after the void nucleation phase are dominated by chemical reactions and/or diffusion processes near the circumference, not by the nature of the defect which nucleated the void.

I. INTRODUCTION

One of the major challenges of high-density integrated circuit technology as well as basic surface science and materials research is the identification of low-density surface and interface defects. In order to identify and characterize low-density defects, they must be made detectable against the overwhelming background, i.e., they have to be decorated. It appears that the decomposition of thermally grown oxides on Si during vacuum anneal decorates defects at the oxide–Si interface or within the silicon near-surface region. Ther- mally grown oxide films on Si decompose at elevated temperatures in oxygen deficient ambient via the reaction SiO$_2$ + Si → 2SiO$_2$. At temperatures above ~800 °C, SiO$_2$ has a non-negligible vapor pressure, which leads to oxide decomposition when SiO$_2$ can escape the Si–SiO$_2$ interface region. Recent work has demonstrated that this process is highly nonuniform: the process is initiated locally; approximate circular voids form in the oxide (exposing the clean Si surface) and grow laterally, while the oxide between the voids remains unchanged.

We have studied the decomposition of oxide films of 50 to 500 Å on Si(100) during the ultra-high vacuum annealing in a scanning Auger microscope. Void growth rates and size distributions are determined to gain insight into the growth mechanism and possible relation to the nature of the defect which initiates the void formation. The void size distribution is found to be strongly peaked, indicating that the major size of voids are nucleated by the same kind of defect. The void diameter (circumference) grows linear with time allowing the conclusion that the oxide decomposition is rate limited by peripheral reaction; e.g., either diffusion (reactants or products) near the periphery of chemical interaction that yields the volatile SiO product.

II. EXPERIMENTAL

Oxide films varying from 50 to 500 Å were furnace grown in dry oxygen at 900–1000 °C on p-type, 2 Ω cm Si(100) wafers. Anneal of the wafers was performed in situ by direct current flow through the samples in the temperature range from 600 to 1200 °C. Molybdenum clamps were used as electrical contacts for the anneal. There is no identification of the clamp material influencing the void growth: the density of voids is uniform across the sample and can be reduced con- siderably by using oxides grown with O$_2$/HCl mixtures. Temperatures were determined with an infrared (IR) pyrometer that had been calibrated with a thermocouple; the accuracy of absolute temperature determination is estimated to be ±25 °C. Temperature gradients along the wafer surface are found to be in the same order of magnitude. The anneal was done in a scanning Auger microscope (SAM) Phi 590 with a base pressure of 5 × 10$^{-9}$ Pa. Magnifications used for imaging were less than 100 ×, corresponding to a field of view of 0.2 mm$^2$ with beam energies around 3–5 keV and beam currents around 10–50 nA. During the course of an experiment the amount of decomposition of the oxide due to the electron beam was found experimentally to be less than one monolayer. Data obtained in an optical microscope agree with those from the SAM, confirming that the influence of the electron irradiation is negligible in this case. Anneals were done either continuously, monitoring the surface with secondary electron imaging (SEM mode), or repet- itively, taking adsorbed current (SEM mode) and Auger mapping (SAM mode) images during or after cooldown of the sample. No influence of repetitive cool/anneal cycling on the void growth rates was observed. Images were taken either on Polaroid photos or on videotape.

III. RESULTS AND DISCUSSION

As a typical example of a SiO$_2$/Si(100) sample annealed in vacuum, a sequence of SEM pictures is shown in Fig. 1. The pictures were taken using the secondary electron imaging mode during anneal to 1050 and 1100 °C, respectively, of a 200-Å-thick oxide film on Si(100).

One sees in the sequence the growth of circular voids (the sample tilt of ~60° makes them appear elliptical) with an areal density of several hundred/mm$^2$. As confirmed by Auger mapping, the voids which appear during the anneal are physical holes in the oxide layer, exposing bare silicon. It is apparent that most of the voids are of approximately the same size. They grow with time/increasing temperature, while few voids are formed with continuing anneal. In addition to those "regular" voids a rather low density of voids (several/mm$^2$) of highly irregular shape forms at much lower temperatures (~800–850 °C). Those voids grow initially quite rapidly to sizes of up to several tens of microns average diameter.
diameter for a 500-Å-thick oxide annealed to 1175 °C. The figure shows a sharply peaked distribution where very few voids have diameters outside a quite narrow diameter range. Furthermore, it is apparent that the void number is nearly unchanged with continuing anneal; very few additional voids can be seen to form after the majority is created, and the number of voids under the peak in the distribution does not change with time. Another important feature is that the growth rate of those voids that open up later than most is the same as the growth rate of the majority; the data points in the figure run parallel to each other. Finally it is apparent that a nucleation stage exists, which requires different times for different defect types.

The sample had been annealed to a somewhat lower temperature before these data were taken in order to nucleate the voids, which explains the size offset at time zero. Statistics in this figure are limited at large void diameters due to void overlap; the disappearance of the smaller void from the plot at longer times also originates in this overlap.

This particular plot demonstrates that the voids are nucleated by defects. It seems that the majority of the voids on this sample are nucleated by the same defect because they appear at the same time/temperature. Those voids that open up at a later time, at lower density, seem to belong to a different kind of defect that is less efficient during the nucleation phase. The identical growth rates after the nucleation phase are a strong indication that the growth phase is not dependent on the nature of the defect responsible for the nucleation of the void.

The dependence of the void diameter on annealing time is shown in Fig. 3 for a 500-Å-thick oxide for different annealing temperatures ranging from 1000 to 1175 °C. Only data for the voids from the peak of the size distribution are represen-

Fig. 1. A sequence of scanning electron microscope pictures taken during ultrahigh vacuum anneal of a 200-Å SiO₂ layer on Si(100). The field of view is -0.1 × 0.1 mm, the sample being tilted by -60° giving the circular voids an elliptical appearance. The pictures were taken at 3-keV electron energy and 50-nA beam current in secondary electron mode. The dark voids represent clean Si areas, the bright background the SiO₂ layer. (a) Sample after 5-min anneal to 1050 °C; (b) after additional 3 min at 1100 °C; and (c) after another 7 min at 1100 °C. All three sections show the same sample area.

Sequences of images like the ones shown in Fig. 1 were used to derive growth kinetics data by measuring diameters and size distributions versus temperature and time for three different oxide thicknesses: 50, 200, and 500 Å. Kinetics data were only obtained for regular-shaped (circular) voids.

Figure 2 shows a three-dimensional representation of the void size distribution versus annealing time and versus void number.

Fig. 2. Three-dimensional plot showing the dependence of void number vs time in minutes and vs void diameter in microns. Data were taken from a 0.7 × 0.3 mm surface area of a 500-Å oxide on Si(100) annealed to 1175 °C. The void density is in the order of 10⁹/mm². The data were obtained from in situ absorbed current images taken during sequential anneal.

Fig. 3. Void diameter in microns vs annealing time for vacuum annealed 500-Å SiO₂/Si(100) samples. The samples had been annealed to temperatures ranging from 1000 to 1175 °C. The data at 1000 and 1175 °C were taken during in situ anneal in a scanning Auger microscope comparing diameters obtained for the same set of voids that grew with time. Different experimental conditions have been used for the 1050, 1100, and 1150 °C data: each data point originates from a separate sample and represents an average over the size distribution measured in an optical microscope (Ref. 2 and private communication). The dashed lines in the double-logarithmic plot represent a linear dependence of the void diameter with the annealing time.
sented in this figure. The double-logarithmic plot shows a linear dependence of the void diameter (circumference) on annealing time for all temperatures studied.

Similar results are obtained for the other oxide thicknesses, the only noticeable difference being faster growth for thinner oxides. A reduction of oxide thickness from 500 to 50 Å yields an about 20-fold increase in the growth rate, i.e., the growth rate scales somewhat slower than inversely proportional to the oxide thickness. The experimental data plotted in Fig. 3 allow an estimation of the activation energy of entire void growth process, which we find to be $2.0 \pm 0.25$ eV.

The range of reliable diameter determinations is experimentally limited at the two extremes: (1) very small holes cannot be observed in situ because an increase of magnification of the SAM would greatly enhance the electron irradiation dose, which might interfere with the void growth; and (2) very large holes tend to overlap strongly. Another complication that makes growth kinetics data for large holes less reliable is temperature instability. In this study the wafers are heated by direct current flow through the sample, and thermal equilibrium is established by heat loss via radiation. During the course of the experiment the average sample emissivity changes corresponding to the ratio of uncovered to covered Si surface. Having a constant energy supply, one expects the temperature of the sample to change when an appreciable percentage of the sample surface is uncovered. No effort was made to correct for this temperature change. We attribute any deviations at the extreme ends of the plot from the linear dependency seen in the center region to experimental errors of these kinds. The data for 1050, 1100, and 1150 °C were obtained using separate wafers for each data point. Additional experimental limitations for such data lie in the limited reproducibility of temperature and oxide thickness from run to run.

It should also be noted that any kind of surface-averaged measurement of the ratio of covered/uncovered surface area is not a reliable source from which to infer growth rates of single voids for two reasons: (1) the opening of large irregular voids at low temperatures, i.e., any kind of distribution of defect sizes, and (2) strong overlap for larger void diameters. The nucleation of the low-temperature voids still remains to be explored but can influence several percent of the surface area. We have calculated where void overlap distorts surface-averaged measurements using a random surface distribution of equally sized voids growing in time with the same speed. For the experimentally observed void density range strong influences of void overlap are obtained at void surface coverages as low as 30% (oxide coverage 70%).

The experimental finding of a linear growth of the diameter with time suggests an important conclusion concerning the growth mechanism. Linear growth of the diameter indicates a reaction that is rate-limited at or near the circumference, i.e., the interface between the existing oxide and the newly exposed silicon surface. Such growth behavior is independent of the nature of the defect which initiated the void. This can be seen in Fig. 2, where different voids show the same growth rate once they have been nucleated; only the time required to nucleate them is different.

The separation of nucleation and growth stages is particularly clear from the data here. It may be useful to think of the nucleation stage in two steps. In step (1) a defect enables the creation of the volatile reaction product SiO, e.g., via interfacial reaction catalyzed by the peculiar bonding at the defect site. This defect may well be located near the SiO$_x$/Si interface, where an almost infinite supply of the two reagents Si and SiO$_2$ exists. In step (2) the amount of SiO accumulates with time and begins to penetrate and stress the SiO$_2$ overlayer. The time required for this step depends on the integrity and thickness of the oxide. The nucleation stage may be manifested by a deterioration of the electrical properties of the oxide because unsaturated bonds accumulate in the near-interface region.

In the void growth stage, a continuous path has already been created from the bare Si surface to the oxide surface, allowing the reaction product SiO to escape easily. The effectiveness of the defect as a SiO source ultimately determines the thermal load necessary to create sufficient SiO to penetrate the overlying oxide. Thus thinner oxides should exhibit a greater variety and number of voids, since even less effective defects may create enough SiO to break and/or diffuse through such an oxide. We find experimentally that the density of voids observed for different oxide thicknesses increases with decreasing oxide thickness, supporting the above ideas. For very thin oxides (less than ~20 Å) one might expect that the voids decorate micropores present in very high density in thermal SiO$_2$.

Beyond the initial nucleation phase the void growth reaction seems to reflect no further information about the nature of the original defect. The growth of the void diameter (circumference) is thought to be an interfacial reaction consisting of three steps: (1) diffusion of the reaction products to the reaction site, (2) chemical reaction forming SiO$_2$, and (3) evaporation of the reaction product SiO. Since the activation energy of ~2 eV found for void growth is notably less than the 3.9-eV$^*$ value characteristic of the growth and decompo-

![Cross-sectional TEM micrograph for ultrahigh vacuum annealing of a 300-Å SiO$_2$ layer on Si(100). 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 glass used in the sample preparation. The figure represented from Ref. 1 is with permission of the authors.](image-url)
sition of ultrathin oxides under reduced pressure or of the SiO equilibrium vapor pressure, step (3) (SiO evaporation) can be ruled out as the rate-limiting step in void growth. If the reaction rate were not limited at least partially by diffusion one would expect void growth independent of the oxide thickness and thinning of the oxide remaining between the voids, because Si could move freely over the void sidewalls and the oxide surface. Cross-sectional transmission electron microscope (TEM) pictures of a void as in Fig. 4 show that the reaction occurs all along the oxide sidewall, but with significant undercut at the Si–SiO₂ interface. At the same time, medium-energy ion scattering (MEIS) data demonstrate that thinning is negligible for the majority of the remaining oxide areas. We therefore conclude that diffusion of the reaction partners to the reaction site plays an essential role in determining void growth rates. This does not preclude some additional influence of the SiO reaction on the growth rate.

We have also found that linear growth of void diameter versus time dominates void growth kinetics for oxide films on poly-Si as well, with growth rates very similar to those on Si(100). Because poly-Si exposes a wide variety of grains at surface and interfaces, the similarity of oxide decomposition kinetics on poly-Si and single-crystalline substrates underscores that local or interfacial structural details do not interfere significantly with oxide decomposition rates. Void nucleation in oxides has been observed to be enhanced when metal impurities are present in the silicon. Since dry oxidation (with no HCl) used here gave a very high areal density of voids compared to O₂/HCl grown oxides it is clear that metal impurities can serve as nucleation centers for void growth.

ACKNOWLEDGMENTS

We gratefully acknowledge fruitful discussions with K. Hofman, M. Bradley, P. Gas, F. d’Heurle, and J. Philibert. The help of J. Calise, S. Cohen, and D. Quinlan is greatly appreciated.