SiO₂/Si Interfaces Studied by STM

Masaaki Niwa and Hiroshi Iwasaki
Semiconductor Research Center
Matsushita Electric Industrial Co., Ltd.
3-15 Yagumo-nakamachi, Moriguchi, Osaka 570 Japan

Topologies of SiO₂/Si(100) interfaces grown by several oxidation conditions have been observed using Scanning Tunneling Microscope (STM). Hydrogen terminated Si surfaces that were checked by XPS and AES were used. The interfaces showed ripple-like corrugations that consist of steps. The large step height was produced by wet oxidation. Morphologies of the interfaces measured by STM are consistent with the observation by TEM.

1. INTRODUCTION

It is quite important to study SiO₂/Si interfaces which affect important characteristics such as FDDB, TDDB, and carrier mobilities of MOS FET.

In this work, we study some practically important SiO₂/Si interfaces, i.e., conventional gate oxide layers grown to 10 nm thick in dry O₂, 16 nm thick in wet O₂ and LOCOS field oxide layer with 600 nm thick. SiO₂/Si interface observation by means of STM in air with proper chemical surface treatments revealed characteristic interface topographies that are very important in LSI’s.

2. EXPERIMENTAL

2.1 Sample preparation

P-type, 6-inch Si(100) substrates with resistivity of 10–13 Ωcm were cleaned by RCA method¹ to remove native oxide and contaminants on the surface. After RCA cleaning, Si substrates were oxidized in a quartz tube which had been cleaned at higher temperatures and by a controlled ambient. Oxidation conditions are as follows,

Sample A : SiO₂ of 10 nm thickness (Gate oxide) was thermally grown in dry oxygen ambient on the Si substrate at 900°C for 25 min.
Sample B : SiO₂ of 16 nm thickness (Gate oxide) was thermally grown in wet oxygen ambient on the Si substrate at 900°C for 11 min.
Sample C : SiO₂ of 600 nm thickness (LOCOS field oxide) was thermally grown in wet oxygen ambient on the Si substrate at 1000°C for 175 min.

As for sample D, LOCOS active area with the gate oxide layer was grown to 16 nm thick in wet oxygen and 330 nm of gate poly silicon electrode was formed.

To improve the quality of SiO₂ film, samples have been annealed in dry N₂ gas for 20 min successively after the oxidations. Oxide thicknesses of the above samples have been measured with an ellipsometer.

Practical cleaning method to prevent oxidation in air without a damage against the interface morphology after removal of oxide²,³ has been adopted. The H-terminated Si surfaces have been prepared by
etching the SiO₂ layer by means of being dipped into pure HF (5%) solution and then rinsing briefly in deionized water. Finally, the Si surface was dried by blowing dry N₂ gas. The H-terminated surfaces have been reported to show an interface state density lower than that obtained at the SiO₂/Si interface².

Time dependence of oxidation of the H-terminated Si surfaces has been measured by XPS (X-ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy).

2.2 Measurement of STM, TEM, XPS and AES.

After removal of oxide, these Si chips have been immediately set in a STM glovebox that is continuously purged by dry N₂ gas at atmospheric pressure.

A three dimensional tube type piezo scanner with a Pt/Ir tunnel tip has been used here. At the same time, oxidations of Si surface have been measured by XPS, and AES. Samples have been stored in air during the intervals of the XPS measurements.

TEM (Transmission Electron Microscope) observations of SiO₂/Si interfaces have been also done.

3. RESULTS and DISCUSSION

3.1 Oxidation

Figure 1 shows time dependence of O/Si atomic ratio of sample A measured by XPS. The surface has been found to be passivated well in comparison with high temperature treated silicon surface⁴). As is shown in figure 2, AES spectrum measured simultaneously with the XPS indicates the existence of Si-H bonds at HF dipped surface by means of "finger print" proposed by Madden⁵).

Fig.1 Time dependence of reoxidation measured by XPS for HF dipped Si surface (sample A).

From these results, surface chemical preparation used in this experiment was found to be suitable for terminating the dangling bonds by hydrogen atoms.

3.2 Morphology

STM topographies of the SiO₂/Si interfaces prepared by the above method are shown in figures 3 through 5. Figure 3 shows the STM image of the sample A. The topogram shows fairly flat surface in the area of about 1μm² except for fine rippled corrugations with short periods (≈300Å in length) and small amplitudes of less than 10Å.

Figure 4 is the STM image of the sample B. In this case, the interface has the ripple like morphology with the typical sizes of about 40Å in height and periods of about 500-800Å in length.

Fig.2 AES signals of Si-Si and Si-H as references of the HF dipped Si surface (sample A).
Tunneling current of 0.50nA was also stable and STM images obtained were quite reproducible during the observations both for figures 3 and 4. Similar kind of morphology to sample B has been obtained as for LOCOS active area, sample D.

It has been clarified that these slopes of vicinal ripple like steps are the real corrugations of the interfaces3).

As for sample B and D, in general, the interface roughness on height and period is apparently larger than that of sample A. The physical reason for this difference is considered to be high oxidation rate due to water in wet ambient which may cause summing up each steps, hence larger steps with longer periods than in dry oxygen. And that, the average inclination angles of steps of both sample A and B were approximately 2-4° respectively estimated from the typical configurations. And from the results of optical imaging method, the inclinations have turned out to be approximately 1.6-3.1° and 2.3-3.5° for samples A and B respectively. Considering the observational error, these results fairly coincide with the inclination angles observed by STM.

According to the discussions above, these microscopic slopes of the surface may be due to misorientation of the Si single crystal.

In contrast, for the case of sample C, the STM image shows a quite different feature (Figure 5). Wide terrace like steps with ~100Å height and periods of greater than ~1200Å could be observed rather than ripple like steps.

We have also examined these SiO2/Si interfaces by cross sectional high resolution TEM. Figure 6 shows the cross

Fig.3 STM image of SiO2(10nm in dry O2)/Si interface (sample A).
Xfull=9300Å, Yfull=8400Å, Z(Y)=417Å/div.
It=0.50nA, Vs=1.50V

Fig.4 STM image of SiO2(16nm in wet O2)/Si interface (sample B).
Xfull=9300Å, Yfull=8400Å, Z(Y)=417Å/div.
It=0.50nA, Vs=1.78V

Fig.5 STM image of SiO2(600nm in wet O2)/Si interface (sample C).
Xfull=9300Å, Yfull=8400Å, Z(Y)=1250Å/div.
It=0.50nA, Vs=0.66V
sectional view of SiO2/Si interface of the sample A. The roughness is smooth over the interface and very sharp and straight boundary between Si and SiO2 with less than 10Å undulation. As for the sample B, the SiO2/Si interface shows different feature (Figure 6). The interfaces are undulating roughly with a maximum excursion of about 35Å. Considering that the lack of distinct period is thought to be due to cross sectional overlap, these results are consistent with the STM results described above.

The STM images discussed above are consistent with detail investigations by Hahn and Henzlar who have reported that wet oxidation resulted in higher roughness than dry one6).

4. CONCLUSION

The morphologies of SiO2/Si interface observed by STM has been consisted of fine rippled corrugations with less than 10Å height and short period length(≤300Å) in case of dry oxide interface. As for the interfaces of both wet oxide and wet oxide formed on LOCOS active area, inclined rippled morphology with lager undulations and periods(≈40Å in height and 500~800Å in length respectively) have been observed. Misorientation of silicon single crystal is considered to cause the inclination(2~4°) of these rippled steps and large step height, hence long period is thought to be produced by wet oxidation.

In case of LOCOS field oxide, the interface seems to show terrace like morphologies with higher step height (~100Å) and flat surface with large periods (≥~1200Å). Further investigation will be needed for the cause of the "huge" terrace.

SiO2/Si interface topologies observed by STM are consistent with the cross sectional observations by TEM.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge Dr. S. Horiuchi and Dr. T. Takemoto for encouragements for this work.

REFERENCES