Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 95-97

Invited

Characterization and Control of Native Oxide on Silicon

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Characterization and control methods of native oxide growth on silicon (Si) surfaces at room temperature and during the temperature ramp-up are described. The native oxide growth on HF-cleaned Si surfaces can be controlled by lowering oxygen or water concentration in process ambience at room temperature and by passivation of Si surface for semiconductor processes at temperatures higher than 300 °C. In situ control methods of native oxide growth for semiconductor processes are developed based on analyses of factors dominating the native oxide growth.

1. INTRODUCTION

The characterization and control of native oxide growth on Si surfaces is essential in the fabrication of ultra large-scale integrated devices. The presence of native oxide on Si surfaces degrades low-resistance contact formation, low-temperature growth of highquality epitaxial Si films, and high-quality gate oxide formation. Native oxide is unintentionally grown on Si surfaces under conditions before each process. The native oxides can be classified by growth condition parameters such as temperature and ambience as summarized in Table 1. Here, the uncontrolled oxide grown at elevated temperatures is defined as a type of native oxide.

In this paper, we discuss the factors controlling the native oxide growth in air and in ultrapure water at room temperature¹⁻³⁾ and during the wafer temperature ramp-up in each process system,⁴⁾ and present in situ control methods of native oxide growth in W/n⁺-Si(100) contact formation,⁵⁾ low-temperature Si epitaxy,⁶⁾ and very thin gate oxide formation^{7,8)} processes.

Table	1.	Various	native	oxides.
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Ambience	
Air	
Ultrapure water	
Chemicals	
Process gas, Vacuum	

2. NATIVE OXIDE GROWTH AT ROOM TEMPERATURE

The native oxide can be quantitatively analyzed by xray photoelectron spectroscopy (XPS).²⁾ Figure 1 shows Si_{2p} XPS spectra measured for native oxides on HF-cleaned n-Si(100) surfaces exposed to air at room temperature for various lengths of time, where the take-off angle of photoelectrons is 35°. The oxidation-induced chemicallyshifted peak is easily observed after exposure to air for 1440 min (1 day), indicating that the native oxide grows for the initial exposure time. The peak from native oxide for 2880 min (2 days) overlaps with that for 1440 min (1 day). The native oxide growth for the additional exposure time of 1440 min (1 day) is minimal. The peak intensity increases during the period from 2880 min (2 days) to



Fig.1. Si2p XPS spectra of native oxides on n-Si(100) surfaces exposed to air at room temperature.



Fig.2. Contact resistances of W/n^+ -Si(100) for contact areas.

21600 min (15 days). The peak does not change during the additional exposure of 21600 min (15 days). Therefore, XPS measurements clearly exhibit the step-wise increase in the native oxide thickness.

The amount of native oxide can be expressed as the film thickness by the calibration of the intensity ratio of Si_{2n} XPS signals from oxide to that from the Si substrate with thermal oxide film thickness measured by ellipsometry.²⁾ The native oxide grown in air indicates a successive step-functionlike increase in native oxide.2) This is also observed in the measurement of physical thickness with atomic force microscope (AFM) calibrated by ellipsometry.9,10) These results suggest that layer-by-layer oxide growth occurred on HF-cleaned Si surfaces at room temperature. The native oxide hardly grows at all in air when the H₀ concentration is suppressed bellow 0.1ppm.²⁾ This shows that the native oxide growth on the HF-cleaned Si surface at room temperature requires the coexistence of oxygen and moisture.

The oxide thicknesses on n-Si wafers in ultrapure water at room temperature increase with increasing immersion time and dissolved oxygen concentration.²⁾ This result suggests that the native oxide growth is suppressed in ultrapure water by decreasing the dissolved oxygen concentration. The initial growth rate of native oxide on n⁺-Si is very high. The oxide thickness on n⁺-Si also reduces as the dissolved oxygen concentration decreases.²⁾

3. OXIDATION AFTER HYDROGEN THERMAL DESORPTION

The thermal desorption spectra of hydrogen, oxygen and water from the HF-cleaned Si surface indicate that hydrogen is desorbed at about 300°C and



Fig.3. Reflection electron diffraction patterns of phosphorus-doped Si films on Si(100) substrates at 550°C (a) with and (b) without Si_2H_6 gas molecular-flow pre-showering.

has peaks at 400°C and 520°C, and intensities for both oxygen and water decrease at approximately 500°C and 800°C.⁴⁾ The thermal desorption characteristics of hydrogen from the HF–cleaned Si surface in one atmospheric pressure Ar gas is reported to be similar to that in vacuum.¹¹⁾ The increase of oxygen concentration on the Si surface at about 500°C, as measured by XPS, coincides with the first consumption of oxygen and water.⁴⁾ These results indicate that the desorption of hydrogen from the HF–cleaned Si surface occurs from about 300°C, and that the Si surface reacts with oxygen and water at temperatures higher than 500°C.^{12,13)}

4. NATIVE OXIDE CONTROL IN SEMICONDUCTOR PROCESSES

Figure 2 shows contact resistances of W/n⁺–Si(100) contact areas. In a nitrogen gas sealed process, the Si wafer is chemically etched with diluted HF acid, rinsed in water with low dissolved oxygen concentration(20 ppb), and dried by N₂ gas blowing in N₂ sealed wet cleaning equipment,¹⁴⁾ and then transported by N₂ wafer carrier to the chemical vapor deposition (CVD) system, in order to suppress native oxide growth in ultrapure water and in gas ambient. In a conventional process, HF dipping, ultrapure water rinsing, N₂ gas blowing and wafer transportation are carried out in clean room air. The resistance of the contact formed by the nitrogen gas sealed process is smaller than is seen in the conventional process, as reported for Al/n⁺– Si(100).¹⁴

Figures 3 (a) and (b) show reflection electron



Fig.4. Current density-electric field characteristics of n^+ -polycrystalline Si/SiO₂/p-Si(100) diodes under negatively biased metal electrodes for 6.2 nm ultraclean oxides.

diffraction (RED) patterns of phosphorus-doped Si films formed on Si(100) substrate at a temperature of 550 °C with and without Si₂H₆ gas molecular-flow pre-showering in a CVD system, respectively.⁶ The Si₂H₆ pre-showering is started at temperatures in the vicinity of 520 °C, at which coverage of hydrogen atoms terminating the Si atoms at the substrate surface drastically decreases due to thermal desorption of the hydrogen.⁴ The diffraction pattern of the film formed with Si₂H₆ gas molecular-flow pre-showering clearly indicates a Kikuchi line. Good crystallinity of phosphorus-doped Si film can be obtained by using PH₃ pre-showering.⁶ These results are due to suppression of the oxide growth by passivation of the Si surfaces during the temperature ramp-up.

Figure 4 shows the effect of the preoxide thickness in ultraclean oxide^{7,8,15}) on the current density-electric characteristics field of n+polycrystalline-Si/SiO₂/p-Si(100) metal-oxidesemiconductor(MOS) diodes, where the preoxide is defined as an oxide grown during the wafer thermal ramp-up oxidation temperature to temperature. Preoxide with 0.4 nm thickness is intentionally formed at 300°C for passivation,¹⁶⁾ and subsequently the temperature is ramped up in an ultraclean Ar gas to prevent oxide growth and an increase in surface microroughness before thermal oxidation. The current level for the ultraclean oxide with 0.4 nm preoxide is lower than that of the ultraclean oxide with 3.0 nm preoxide over the range. This result shows that the presence of preoxide in very thin gate oxide films induces the degradation of the electrical insulating performance.

5. CONCLUSION

In situ control methods for the native oxide growth on Si surfaces are developed based its ability for the enhancement of process performances. In situ control methods require no additional process step. Consequently, these methods promote high performance processing and investment savings.

ACKNOWLEDGEMENTS

The authors are grateful to K. Suma, E. Hasegawa, K. Yamada, M. Kawakami, M. Ohwada, A. Teramoto, C. M. Soh, H. Suzuki, K. Makihara, K. S. Tseng, Y. Maeda, T. Sako, K. Nakamura, M. Y. Kwon and R. Au of Tohoku University, Dr. N. Yabumoto and Dr. K. Saito of NTT LSI Laboratories, and Professor T. Hattori of Musashi Institute of Technology for their help in this work and useful discussions. The majority of this work was carried out at the Super Clean Room of the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University. This work was partially supported by the Grant–in–Aid for Scientific Research (No. 04452166) from the Ministry of Education, Science and Culture of Japan.

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