Effect of Silicon Wafer In-Situ Cleaning on the Structure of Ultrathin Silicon Oxide Films

Naotomi TERADA, Hiroki OGAWA, Kazunori MORIKI, Akinobu TERAMOTO, Koji MAKIHARA, Mizuo MORITA, Tadahiro UMI and Takeo HATTORI

Department of Electrical and Electronic Engineering, Musashi Institute of Technology, Setagaya-ku, Tokyo 158
*Department of Electronics, Tohoku University, Sendai 980

The chemical structures of thermal oxides were found to be affected strongly by the condition of silicon wafer in-situ cleaning. Based on this phenomena, the optimum condition for decomposition of native oxides was investigated. In the case of heating native oxides at 900 °C, the optimum condition for obtaining smooth and clean surface could not be found. The minimum amount of suboxides were found in thermal oxides when the native oxides formed in a solution with composition of HCl:H2O2:H2O=1:1:1 maintained at 90 °C were decomposed at 850 °C.

1. INTRODUCTION

In order to form ultrathin silicon oxide films with high quality, the thickness of native oxide formed before thermal oxidation should be minimized or the structure of native oxides should be optimized. The decomposition of native oxides at high temperature in high vacuum was first studied by Ishioka and Shiraki in order to obtain contamination free silicon surface. Here, a mixed solution of HCl, H2O2, and H2O was used to form native oxides. This cleaning procedure is usually called as Shiraki's method. The decomposition temperatures of various native oxides were measured during wet chemical treatments were studied by Kobayashi et al. by measuring thermal desorption of SiO from native oxides. In the present paper the thermal decomposition of native oxide in high was investigated by measuring the chemical structures of ultrathin silicon oxide films, which were thermally grown after the thermal decomposition of native oxides.

2. Experimental Details

The native oxides studied were formed on (100) surface in a solution with a composition of HCl:H2O2:H2O=1:1:1 maintained at 90 °C after applying modified RCA standard clean. After these native oxides were heated at 900 °C in high vacuum, silicon oxides with thickness of nearly 1.5 nm were formed by ultraclean oxidation method at 800 °C. Heating times at 900 °C were 10, 20, 30 and 60 minutes. The thermal oxide, which was formed at 800 °C by ultraclean oxidation method after removing 200 nm thick thermal oxide formed in dry oxygen at 1000 °C by dilute HF, was used to clarify the effect of thermal decomposition of native oxide on the chemical structures of thermal oxide.

Angle resolved Si2p, O1s and C1s spectra were measured at take off angle of 90, 10 and 2 degrees with acceptance angle of 3.3 degrees by using Scienta ESCA 300. The roughness at silicon oxide/silicon interface was measured by scanning tunneling microscope (STM) after removing thermal oxides by dilute HF.

3. Experimental Results and Discussions

Fig. 1(a), 1(b) and 1(c) show Si2p photoelectron spectra measured at photoelectron take off angle of 90, 10 and 2 degrees, respectively. Spectra denoted by a were measured for thermal oxide with thickness of nearly 1.5 nm and are used as reference spectra. Spectra denoted by b, c, d and e in these figures were measured for thermal oxides with thickness of nearly 1.5 nm after decomposition of native oxides for 10, 20, 30 and 60 minutes, respectively. In order to show the change in the amount of suboxides, whose binding energy is between that of Si in silicon substrate and that of Si in silicon dioxide, the spectral intensity, No, for silicon in silicon dioxide are adjusted to be equal to each other.

In Fig. 2 the spectral intensity, NI, for silicon in silicon suboxide deviated by NO are shown as a function of heating time with take off angle as a parameter. Because the effective electron escape depth is different for three take off angles, the effect of heating on the amount of suboxides near the interface, that is
Fig. 1 (a) Si2p photoelectron spectrum measured at take off angle of 90 degrees.

Fig. 1 (b) Si2p photoelectron spectrum measured at take off angle of 10 degrees.

Fig. 1 (c) Si2p photoelectron spectrum measured at take off angle of 2 degrees.

Fig. 2 Dependence of (NI/NO) on heating time at 900 °C. See the details in the text.
the oxide and that on the surface can be estimated from the dependence of (NI/NO) on three take off angles of 90, 10 and 2 degrees, respectively.

Fig. 3 shows the STM profiles of interface roughness for five kinds of thermal oxides: profile denoted by (a) corresponds to spectrum a in Fig. 1, that denoted by (b), (c), (d) and (e) corresponds to spectrum b, c, d and e in Fig. 1, respectively. Roughness determined by the difference between maximum and minimum height on the wafer in Fig. 3 was found to be well correlated with the amount of suboxides shown in Fig. 2.

The large amount of suboxides on the surface of the oxide film observed for heating time of 10 and 20 minutes in Fig. 2 can be attributed to the imperfect decomposition of native oxides because of short heating time.

Because it is difficult to form near perfect thermal oxides after the decomposition of native oxides at 900 °C, the decomposition of four kinds of native oxides at 850 °C were studied. Consequently, the amount of suboxides in thermal oxide were found to be minimized if the native oxides are formed in a solution with composition of HCl:H₂O₂:H₂O=1:1:1 maintained at 90 °C after applying modified RCA standard clean and are decomposed at 850 °C. It was also found that the increase in surface roughness results in the increase in optical absorption in vacuum ultraviolet.

4. Conclusion

The chemical structures of thermal oxides were found to be affected strongly by the condition of silicon wafer in-situ cleaning. Based on this phenomena, the optimum condition for decomposition of native oxides were investigated. In the case of heating native oxides at 900 °C the optimum condition for obtaining smooth and clean surface could not be found. The minimum amount of suboxides were found in thermal oxides when the native oxides formed in a solution with composition of HCl:H₂O₂:H₂O=1:1:1 maintained at 90 °C were decomposed at 850 °C.

References