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Surface Cleaning Effects of Silicon Substrates by ECR Hydrogen Plasma on Subsequent Homoepitaxial Growth

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Abstract. We have demonstrated the preparation of the almost defect-free homoepitaxial layer and the defective layer, respectively, with and without applying the in-situ cleaning of the silicon substrate surface using electron cyclotron resonance hydrogen plasma. Secondary ion mass spectroscopy indicated that the interfacial oxygen and carbon concentrations, respectively, decreased and increased with the in-situ cleaning. We have investigated the effect of process parameters such as microwave power, d.c bias, and cleaning time, on the epitaxial growth, by evaluating the cross-sectional transmission electron microscopy images of the subsequently deposited Si homoepitaxial film.

Introduction

As device dimensions are reduced into the sub-micron region in pursuit of higher integration density and better circuit performance, low temperature processing, including low temperature cleaning and low temperature epitaxial growth, becomes important. The reduction in process temperature may suppress the dopant diffusion so that the abrupt transition regions can be obtained. In order to achieve high-quality epitaxy with low temperature processing, the technique of in-situ plasma cleaning has been developed [1-4]. Although there have been numerous reports on silicon (Si) homoepitaxial growth at low temperatures [5-13], there are rare reports on the utilization of the electron cyclotron resonance (ECR) plasma cleaning technique and the systematic studies of the effect of the cleaning process parameters on the structural quality of the subsequently grown epitaxial film. In this study, we have performed the in-situ ECR plasma cleaning at 600℃ in order to reduce the interfacial contaminants and we have investigated the structural quality of the silicon epitaxial layer. Since the major surface contaminants of the Si substrate in this study was found to be oxygen and carbon, in order to reduce the possible damage to the substrate, we have used hydrogen gas, which is the lightest element and is reported to react chemically with oxygen or carbon. The ECR plasma system was selected because it can deliver a higher density of low energy ions to the wafer, defeating the disadvantages of using the light hydrogen gas.

Experiments

Substrates were 4 inch, czochralski-grown, p-type (100) Si with 0.5 - 20Ω-cm resistivity. The wafers were RCA cleaned and HF dipped for 20-30 seconds in 10:1 aqueous solutions and rinsed in DI (deionized) water and then dried by manually blowing nitrogen on them. All the processes were done inside the class 100 cleanroom and it took only 10 seconds to load the wafer into the Load Lock Chamber of the chemical vapor deposition (CVD) reactor after the wafer was blow-dried. After the wafers were transferred and loaded onto the heater stage, the main chamber was pumped down and ultimately 1-2 x 10^{-8} Torr could be attained.

In-situ predepositon wafer cleaning was done by using the ECR hydrogen plasma. The ECR was operated at the 2.45 GHz S-band microwave frequency. We applied the in-situ plasma cleaning process with a microwave power of 150-300W, d.c. bias of 10-30V, in-situ cleaning time of 2-5 minutes, pressure of 1 mTorr, and the cleaning temperature of 600℃ and subsequently have deposited the silicon epitaxial layer. Depositions were performed at a temperature of 600℃ by flowing 10 sccm of SiH_4 without carrier gases, immediately after the plasma was extinguished.

A transmission electron microscopy (TEM: JEOL 200CX) was used to observe the epitaxial layers and the epilayer/substrate interface. A secondary ion mass spectroscopy (SIMS: Perkin Elmer 6600) measurement was carried out for detecting surface contaminants, such as carbon and oxygen.

Results and discussion

In order to investigate the effect of the in-situ plasma cleaning on the structural quality of the epitaxial layer, we prepared three samples. Fig. 1a and 1b shows the samples in which no in-situ plasma cleaning was performed. Furthermore, the sample in Fig. 1a was kept for several hours before the deposition, while the sample in Fig. 1b was delivered to the CVD chamber almost immediately after the drying process. Fig. 1c shows the pre-treated sample with the optimized in-situ plasma cleaning process, in which the microwave power, d.c. bias, and cleaning time, respectively, were set to 300W, 10V, and 5 minutes. Cross-sectional TEM images indicate that the in-situ plasma cleaned sample shows a highly crystalline epitaxial layer with an almost invisible epilayer/substrate interface, while the samples without in-situ cleaning showed defective films. We found that the defects were mostly generated from the interfaces and the amount of defects increases with increasing exposure time to air.

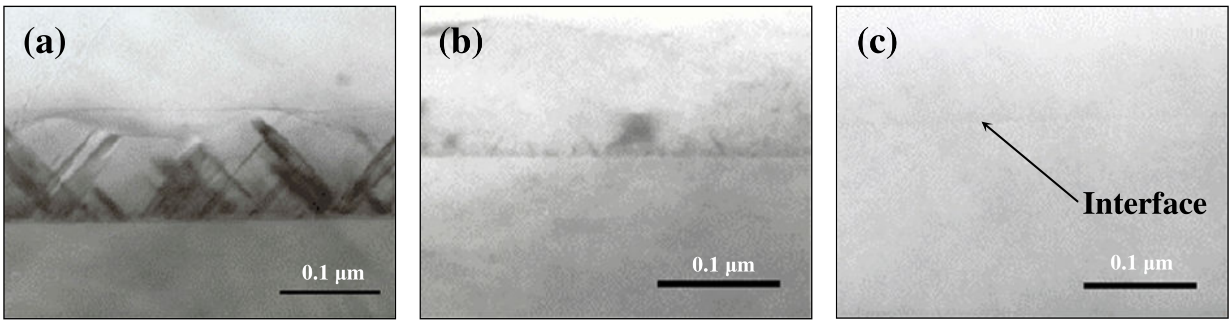

Fig. 1. Cross-sectional TEM images of Si films (a,b) without and (c) with the in-situ cleaning. The substrates were delivered to the deposition chamber (a) with several hours' air exposure and (b) with few seconds' air exposure after the ex-situ surface treatment.

In order to investigate the relation between the defects and surface contaminants, we performed the SIMS measurments. Areal densities of carbon and oxygen were measured by integrating their areas under the interfacial peaks in SIMS depth profiles. Table 1 shows the SIMS data representing the areal densities of carbon and oxygen at the epilayer/substrate interface. After several hours' air exposure, the surface carbon content decreased, which is surmised to be due to the reaction of surface carbon with oxygen in ambient air, generating the volatile species, while the surface oxygen content increased, probabaly due to the growing of native oxide. The interfacial oxygen and carbon concentrations, respectively, decreases and increases by applying the in-situ plasma cleaning. Previous study revealed that the interfacial carbon concentration did not significantly affect the amount of defects in the epitaxial layer and the interfaces [14]. Since the amount of defects observed from TEM images increases with increasing the interfacial oxygen concentration, we surmise that the existence of surface oxygen is closely related to the generation of defects.

Table 1. SIMS data representing the oxygen and carbon areal densities at the epilayer/substrate interface.

	Oxygen (cm^{-2})	Carbon(cm^{-2})
No in-situ cleaning (several hours' air exposure)	1.8×10^{15}	1.4×10^{13}
No in-situ cleaning (few seconds' air exposure)	1.0×10^{15}	1.1×10^{14}
With in-situ cleaning	4.8×10^{13}	4.5×10^{14}

The carbon content increased by in-situ cleaning. Previous experiments proved that the in-situ cleaning process generated the carbon, which is surmised to come from the hydrogen gas or from inside the reactor, during the plasma cleaning process [15]. By thermodynamical consideration (not shown here), we surmise that the reaction of the surface native SiO_2 with the active atomic hydrogen dissociated from the H_2 gas in the ECR plasma, rather than with H_2 gas itself, plays a crucial role in removing the surface oxygen, as mentioned by the previous report [16]. In order to investigate the effect of process parameter on the in-situ plasma cleaning, we have varied the microwave power, d.c. bias, and cleaning time. Fig. 2a shows the cross-sectional TEM images of Si film when the microwave power was set to 150W, with the other process variables the same as the optimized in-situ cleaning condition. The defects are found to generate from the interface when the microwave power decreases from the optimized 300W to 150W, possibly due to the reduced cleaning species. Fig. 2b shows the cross-sectional TEM image of Si film when the bias power was set to +30V, with the other process variables the same as the optimized in-situ cleaning condition. Although the film is found to be an epitaxial layer with a smooth surface, it had a considerable amount of defects such as stacking faults or threading dislocations, probably initiating from the interface. We surmise that considerable amounts of surface oxygen could not be removed, because the ion bombardment energy was reduced by supplying a positive 30 V of d.c. bias. Fig. 2c shows the cross-sectional TEM image of Si film when the cleaning time was 2 minutes, with the other process variables the same as the optimized in-situ cleaning condition. The image shows broad (about 200Å) interfaces. In some positions on the epilayer/substrate interface, defects are found and they are regarded as oxygen-induced stacking faults or dislocations. We surmise that the insufficient cleaning time helped to generate the surface-oxygen induced defects. Further study is necessary in order to reveal the mechanism of defect generation.

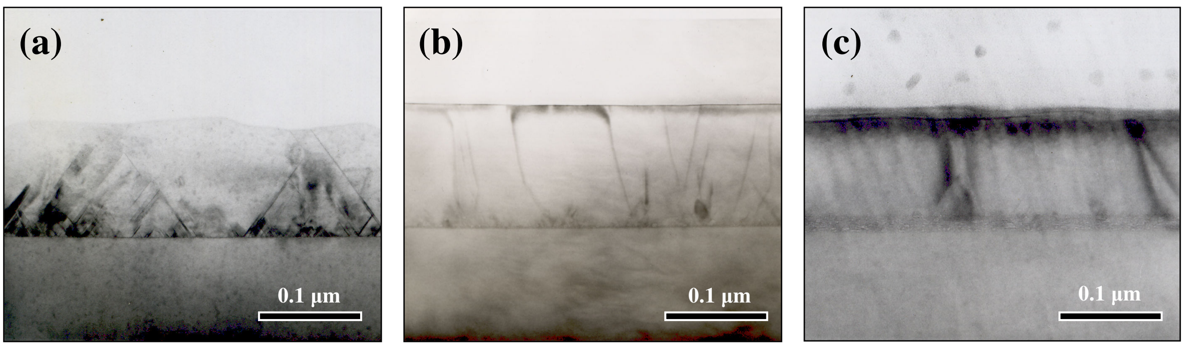

Fig. 2. Cross-sectional TEM images of Si films with (a) the microwave power of 150W, (b) the d.c. bias of +30V, and (c) with the cleaning time of 2 minutes.

Summary

We have in-situ cleaned the Si substrate using ECR hydrogen plasma and subsequently deposited the Si film by flowing SiH_4 without carrier gases at the temperature of 600℃ in a chemical vapor deposition reactor. TEM images indicated that almost invisible interface could be observed between the substrate and the epitaxial layer in the optimized in-situ cleaning process, implying that an almost defect-free epitaxial film had been produced. SIMS data indicate that the formation of a defective epilayer is related to the existence of surface oxygen species. Reducing the microwave power, decreasing the in-situ cleaning time, and increasing the d.c. bias from the optimized condition contribute to generating the defects, which were shown to initiate from the epilayer/substrate interface

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