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Low-Temperature (625°C) Silicon Epitaxial Growth on Silicon Substrates Heated-Up in SiH_4 Atmosphere

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This paper presents a successful technique for low-temperature silicon epitaxial growth. In order to protect silicon surfaces against the native oxide regrowth around 500 ℃ in the LPCVD reactor, we propose that silicon substrates are heated up to the deposition temperature in silicon source gases, such as, SiH4 atmosphere. On the basis of this proposed process, silicon epitaxy was performed onto HF-treated silicon surfaces at 625 ℃ using LPCVD equipment.

I. INTRODUCTION

In silicon epitaxy, native oxides on starting surfaces have been removed at a high temperature (850-1100 ℃) by H2 or silicon source gases [1], where thermal energy has been used to dissociate the reactant molecules. Therefore it is difficult to lower the process temperature of silicon epitaxy. A particularly difficult step is low-temperature surface cleaning.

Recently, the growth of native oxides has been studied by several authors. An silicon surface cleaned by an HF solution is terminated with hydrogen [2]. The oxide regrowth on the silicon surface terminated with hydrogen proceeds over 500 ℃ even in the low partial pressures of O2 and H2O [3]. Taking account of the oxide regrowth over 500 ℃, this paper presents a successful technique for low-temperature silicon epitaxy. A single-crystalline silicon was formed at 625 ℃ onto HF-treated silicon surfaces which were heated-up in SiH4 atmosphere using a low-pressure chemical vapor deposition (LPCVD) equipment, where no high temperature treatment was needed for the surface cleaning.

II. EXPERIMENTAL APPARATUS

In the LPCVD system, gases of SiH4 and N2 are supplied into an reactor, which accommodates plural silicon wafers. The reactor can be evacuated to 3×10^{-3} Torr by a vacuum pump. Since a heater can be moved to the reactor or off it, the wafers are rapidly heated or cooled between room temperature (25 ℃) and a temperature of LPCVD process. The silicon films were deposited in SiH4/N2 atmosphere at 0.2 Torr. The *in-situ* cleaning of native oxides on silicon surfaces was carried out by N2 diluted anhydrous HF (AHF) gas at a reduced pressure (100 Torr) at room temperature.

The silicon films were evaluated by x-ray diffraction measurements and cross-sectional TEM observations.

III. RESULTS AND DISCUSSION

(A) Low-temperature single-crystalline silicon growth by heating-up silicon substrates in SiH4/N2 atmosphere

The 10-20 Ωcm p-type (100) silicon substrates were used in this study. The substrates were pre-cleaned by NH4OH + H2O2, HCl + H2O2, HF + H2O, D. I. water rinse, and dry. From x-ray photoemission spectroscopy (XPS) analysis, the native oxide on the silicon surface was 0.9 Å after the pre-cleaning. The silicon deposition sequences are indicated in Fig. 1. We will refer to them as sequence A, B, C, and D. In all the sequences, silicon substrates were accommodated into the reactor at room temperature.

In the sequence A as a conventional LPCVD process, after a vacuum/N2 purge cycle, silicon substrates were maintained in N2 atmosphere during heating the substrates up to the silicon deposition temperature (625 ℃). Silicon films were deposited in SiH4/N2 atmosphere at 0.2 Torr. In the sequence B, the *in-situ* cleaning of silicon surfaces was carried out by AHF gas at room temperature. Cleaning time was 60 minutes. After a vacuum/N2 purge cycle, the substrates were heated up to 625 ℃ in N2 ambient. Silicon films were deposited in SiH4/N2 atmosphere. From the x-ray diffraction measurements of the silicon films deposited by the processes with and without AHF cleaning (sequence A or B), the (111), (220), and (311) peaks were observed. This fact means that poly-crystalline silicon films were formed on the substrates. The cross-sectional TEM image of the sample deposited by using the sequence B is shown in Fig. 2. In this photograph, we can see that a poly-crystalline silicon film is formed on the silicon surface.

The growth of native oxide has been studied by several authors. A silicon surface cleaned by an HF solution is terminated with hydrogen, as shown in Fig. 3 (a), and is protected against the native oxide regrowth

in room temperature [2]. Yabumoto *et al.* reported that the oxide regrowth on the silicon surface cleaned by an HF solution (terminated by hydrogen) proceeds over 500 ℃ even in the low partial pressures of O_2 and H_2O (4×10^{-9} Torr and 3×10^{-9} Torr) after hydrogen desorption from the silicon surface [3]. From this fact, we consider that, in the conventional silicon deposition sequence, the native oxide could be easily grown by the residual O_2 and H_2O in the reactor during heating the substrates up to the deposition temperature (625 ℃), as illustrated in Fig. 3 (b). Therefore the poly-crystalline silicon film is grown due to the native oxide regrowth on the silicon surface, as shown in Fig. 3 (c). The growth of the poly-crystalline silicon films in the sequence A and B is attributed to the native oxide regrowth on the silicon surfaces.

In order to protect silicon surfaces against the native oxide regrowth, we propose that silicon substrates are heated up to the deposition temperature in silicon source gases after HF treatment. If we supply a silicon source gas, such as, SiH_4 into the reactor below 500 ℃, amorphous silicon deposition starts before the oxide regrowth, as illustrated in Fig. 4 (b). The deposited amorphous silicon is expected to become a single crystal due to the solid-phase epitaxial (SPE) growth with increasing the temperature to around 600 ℃, as shown in Fig. 4 (c). When the SPE growth rate is larger than the deposition rate of amorphous silicon, the SPE growth proceeds up to the film surface of amorphous silicon. After that, the single-crystalline silicon is consecutively deposited on the film surface due to the gas-phase epitaxial growth (Fig. 4 (d)). On the basis of this proposed process, a silicon substrate was heated from room temperature up to 625 ℃ in SiH_4/N_2 atmosphere in the sequence C. The SiH_4 and N_2 flows were 20 and 300 sccm, respectively, and the pressure was 0.2 Torr in the heating step. The deposition rate of amorphous silicon at 500 ℃ was 1.5 Å/min. After the temperature reached 625 ℃, the silicon film was consecutively deposited in SiH_4/N_2 (= 200/300 sccm) atmosphere at 0.2 Torr for 20 minutes. The cross-sectional TEM image of the sample deposited by using the sequence C is shown in Fig. 5 (a) and (b). In these photographs, we can see that a 3200-Å single-crystalline silicon film is grown on a silicon surface. Thus single-crystalline silicon growth was performed onto the HF-treated silicon surface at 625 ℃, where no high-temperature cleaning was used. However we can still observe some defects in the single-crystalline silicon film and at the film-substrate interface.

(B) Silicon surface cleaning by anhydrous HF gas

The film quality of the single-crystalline silicon obtained by the above technique is particularly responsive to the cleanliness of the starting surface. The gas-phase HF cleaning is one of the methods for low-temperature surface treatment [4]. We used a gas-phase AHF cleaning system. The native oxides can be etched by AHF gas in the same reactor with the LPCVD one. As a test of the process, XPS analysis was carried out on silicon surfaces, both with and without the gas-phase AHF cleaning procedure. The AHF cleaning time was 60 minutes. The thicknesses of native oxides were obtained from the Si_{2p} spectra. The native oxide was reduced from 0.9 to 0.2 Å after the gas-phase AHF cleaning, while flourine increases.

We deposited a 2700-Å silicon film *in situ* on a silicon surface that had received the gas-phase AHF cleaning in the sequence D. During heating the reactor up to 625 ℃, the substrate was maintained in SiH_4/N_2 (= 20/300 sccm) atmosphere. After the temperature reached 625 ℃, the silicon film was deposited in SiH_4/N_2 (= 200/300 sccm) atmosphere at 0.2 Torr. The cross-sectional TEM observation was carried out on the deposited substrate with the gas-phase AHF cleaning procedure. We can see from Fig. 6 (a) and (b) an single-crystalline silicon film on the silicon surface. In these photographs, there is no lattice disorders near the interface between the single-crystalline silicon film and the substrate. This result shows that silicon epitaxial growth was performed onto the silicon surface at 625 ℃. Moreover, no defects are observed in the epitaxial silicon film and at the film-substrate interface. Thus at least in sight of cross-sectional TEM observation, the epitaxial silicon film with no defects was obtained at 625 ℃ onto the silicon surface cleaned by the gas-phase AHF treatment by means of heating-up silicon substrates in SiH_4 atmosphere.

III. CONCLUSIONS

Silicon epitaxial growth was performed onto HF-treated silicon surfaces at 625 ℃ by means of heating-up silicon substrates in SiH_4 atmosphere using LPCVD equipment. The epitaxial silicon film was obtained with no defects on an atomic scale on the surface cleaned by the gas-phase AHF treatment in the cross-sectional TEM observation areas.

REFERENCES

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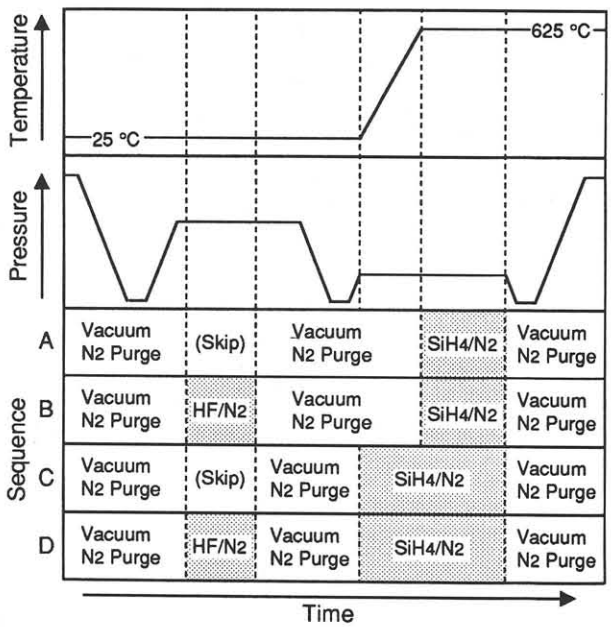

Fig. 1 Process sequences.

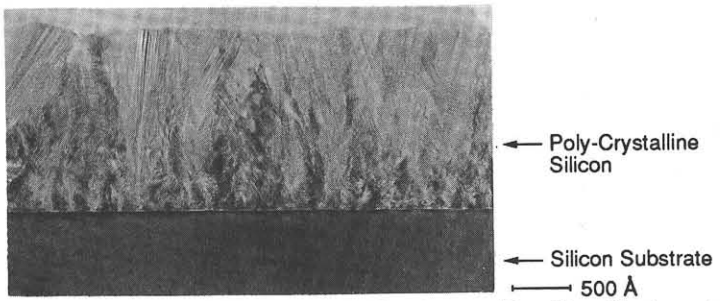

Fig. 2 Cross-sectional TEM micrograph of a poly-crystalline silicon film formed by the conventional silicon deposition sequence.

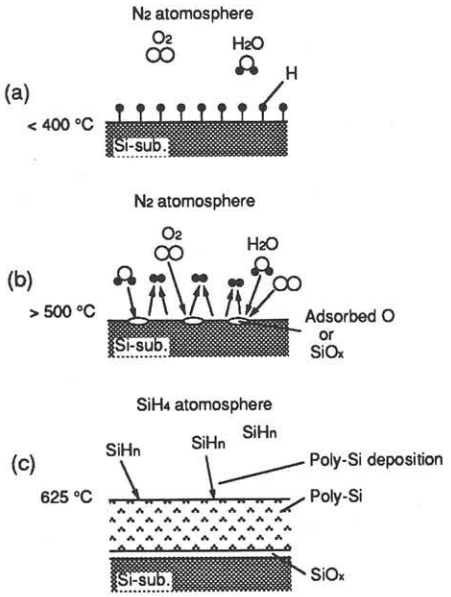

Fig. 3 Schematic drawing of conventional silicon deposition process. (a) A silicon surface cleaned by an HF solution is terminated with hydrogen. (b) The native oxide could be easily grown by residual O_2 and H_2O in the reactor during heating the wafers up to the deposition temperature (625 °C). (c) The poly-crystalline silicon film is grown due to the native oxide regrowth on the silicon surface.

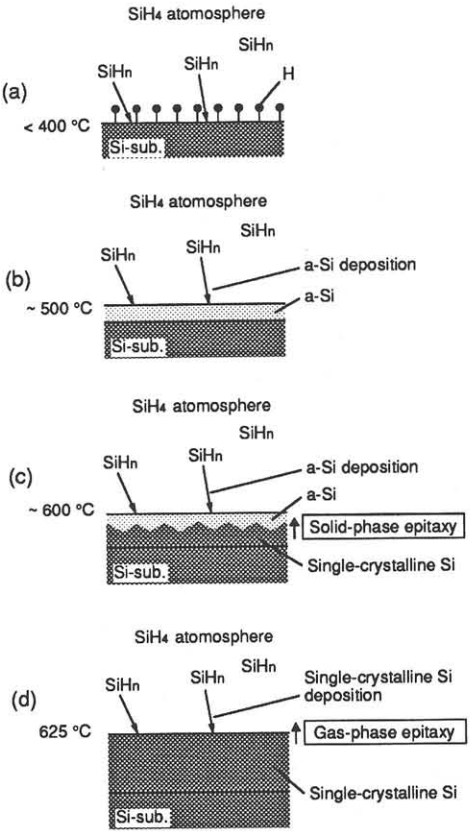

Fig. 4 Schematic drawing of the proposed silicon deposition process. (a) A silicon surface cleaned by an HF solution is terminated with hydrogen. (b) In SiH_4 atmosphere below 500 °C, amorphous silicon deposition starts on the silicon surface before the oxide regrowth. (c) The deposited amorphous silicon becomes a single crystal due to the SPE growth with increasing the temperature to around 600 °C. (d) After the SPE growth proceeds up to the film surface of amorphous silicon, the single-crystalline silicon is consecutively deposited on the film surface due to the gas-phase epitaxy.

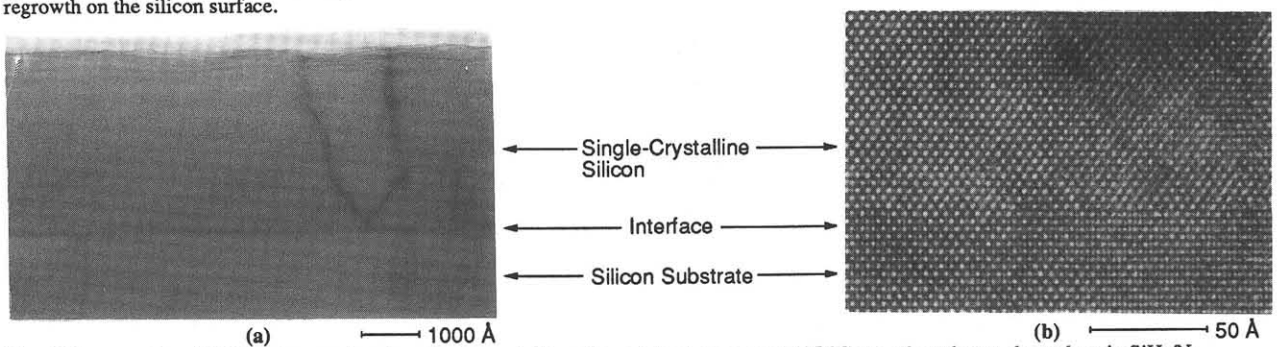

Fig. 5 Cross-sectional TEM micrographs of an single-crystalline silicon film deposited at 625 °C onto the substrate heated-up in SiH_4/N_2 atmosphere. We can still observe defects in the film and at the film-substrate interface.

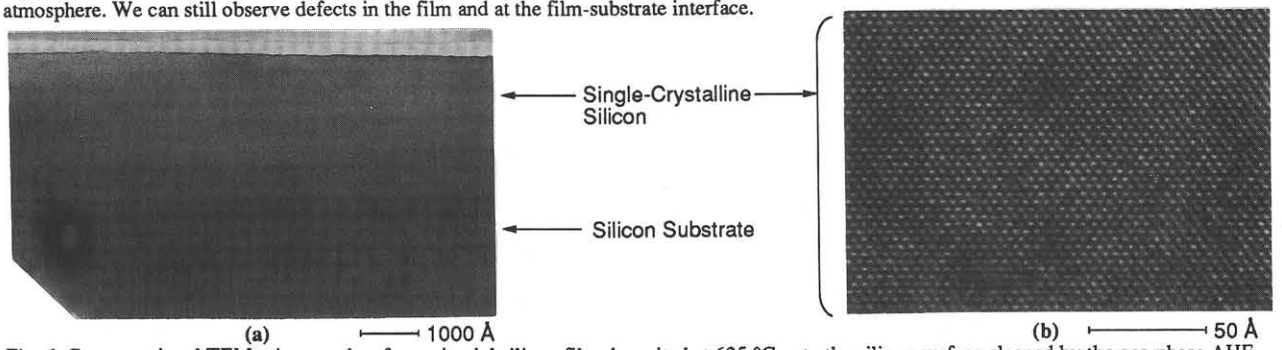

Fig. 6 Cross-sectional TEM micrographs of an epitaxial silicon film deposited at 625 °C onto the silicon surface cleaned by the gas-phase AHF treatment. The single-crystalline silicon film is obtained without defects.