In situ annealing and high-rate silicon epitaxy on porous silicon by mesoplasma process

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By a mesoplasma process, a double-layer porous Si is annealed for a few seconds, by which an annealing effect similar to that of a prolonged conventional annealing process is obtained. The basic annealing process is considered to follow the classical sintering theory. However, the surface of the annealed porous Si is rough with large open voids because of H2 etching. The epitaxial Si films deposited on such a rough substrate at a rate of 350 nm/s show a smooth surface with a low defect density compared with those deposited on a polished Si wafer, which clearly demonstrates the advantages of the cluster-assisted mesoplasma process. © 2016 The Japan Society of Applied Physics

At present, the continuous reduction in the cost of solar cells while maintaining high efficiency is of primary interest in the solar cell industry. One of the effective options is the single-crystal silicon thin-film (scSiTF) solar cell because the cost of this cell could be reduced by reducing the amount of Si while keeping the efficiency of this cell high.1 The main challenge of achieving highly efficient scSiTF solar cells is to develop a cost-effective process to form a Si layer with sufficient crystalline quality. However, crystal Si thin films of <50 µm thickness could not be obtained by slicing. One of the promising attempts is employing a layer-transfer process (LTP) where an active Si layer is epitaxially grown by chemical vapor deposition, which was first proposed by Tayanaka et al.2 Impressively, Solexel has announced its world record conversion efficiency of 21.2% on 156 mm by 156 mm full-square solar cells using a 43-µm-thick epitaxial Si film.3 To produce such scSiTF solar cells at an industry-compatible rate, a high-rate epitaxial growth of single-crystal Si films with an effective LTP is required.4

In conventional approaches, epitaxial Si films are primarily deposited by thermal chemical vapor deposition (TCVD), and a double-layer porous Si is used as a sacrifice layer for layer transfer.3–9 In this process, the porous Si is annealed at hydrogen ambient for more than 30 min at a temperature of ~1100 °C to close the voids on the surface, and the epitaxial Si films are grown at a rate of several 10 nm/s by TCVD from an equilibrium process.6–9 Recently, it has been demonstrated that the mesoplasma CVD (MPCVD) can be used for epitaxial Si film deposition with an ultrahigh rate of ~700 nm/s (from SiHCl3) owing to its unique deposition process, including a high degree of nonequilibrium process, the formation of nanoclusters as deposition precursors, and the instantaneous and simultaneous migration and rearrangement of Si atoms as the clusters impinge on the substrate surface, resulting in high-rate Si epitaxy.10–16 In this process, high-rate and large-area Si epitaxy can be obtained by moving the substrate.17 In addition, mesoplasma has a high number density of atomic hydrogen,18,19 which is considered to be favorable for porous Si annealing.20

In this study, therefore, we employed mesoplasma to investigate the annealing of porous Si and also the Si epitaxial growth on porous Si substrate. The results show that annealing for a few seconds using Ar–H2 mesoplasma has significant effects on the porous Si substrate, similar to those obtained by convention annealing in H2 ambient for >30 min. In this study, the epitaxial Si films deposited at a rate of 350 nm/s on the annealed porous Si substrate from SiH4 show properties identical to those of the films deposited on a polished Si wafer. A one-side-polished, (100)-oriented, p-type monocrystalline Si wafer with a resistivity of 0.01–0.02 Ω·cm was used to fabricate the double-layer porous Si substrate. After being cleaned by an RCA cleaning process, it was set into a custom-designed Teflon cell with a platinum cathode and a Si substrate as the anode. The porous layers were fabricated by galvanostatic mode etching with a mixture of 40% HF acid and ethanol (1 : 1 in volume ratio) as the electrolyte. The porosity and thickness of the porous Si layers were determined from the current density and etching time. In order to obtain porosities of ~20% for the top layer and ~50% for the bottom layer as the conventional porosities of porous Si layers for the LTP process,29 the current densities in this study were selected to be 5 and 200 mA/cm2 for the low- and high-porosity layers, respectively. As a result, the porosities of the layers in this study were 22 ± 3 and 50 ± 2%, respectively, which were determined by a gravimetric method from a single layer.31 The etching time for the low-porosity layer was 200 s and that for the high-porosity layer was 10 s. The corresponding thicknesses of the layers measured from the cross-sectional scanning electron microscopy (SEM) image were determined to be ~1150 and ~750 nm, respectively.

Porous Si annealing and Si film deposition were performed by the mesoplasma process. A porous Si substrate was set on a water-cooled copper holder at a distance from the plasma torch exit of 30 mm. Before processing, the chamber was evacuated to a base pressure of less than 10−4 Pa. The plasma was generated by an RF power (13.56 MHz) with a three-turn water-cooled copper coil. Ar gas with a flow rate of 26 slm and H2 gas with a flow rate of 0.9 slm were used as plasma gases for both porous Si annealing and Si film deposition. The processing pressure was fixed at 800 Pa throughout the experiments. For porous Si annealing, the RF input power...
was gradually increased from 2 to 18 kW within 42 s. This process was basically used to remove the SiO2 layer and heat up the substrate prior to the epitaxial Si deposition in the mesoplasma CVD process.10,16) The Si film deposition started 2 s after the input power reached 18 kW by introducing SiH4 at a flow rate of 100 sccm. The input power was fixed at 18 kW during deposition and the deposition time was 37 s.

The temperature of the substrate was monitored from the bottom of the thermocouple to ensure a good contact with the substrate. A spring system was attached at the bottom of the thermocouple to ensure a good contact with the substrate. In this study, the substrate temperature during annealing was increased gradually from room temperature to ∼800 °C, while it was maintained at ∼900 °C during deposition.

The morphologies of the porous Si before and after annealing and also of the deposited Si films were observed by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800). The structures of the porous Si and Si films were investigated by Raman spectroscopy (Raman, Renishaw Via Reflex) at room temperature with a laser of 532 nm wavelength and also by X-ray diffraction (XRD; Bruker D8 advance) and electron backscatter diffraction (EBSD; FEI Quanta FEG 250). The surface roughness was measured by atomic force microscopy (AFM) using a scanning probe microscope (SPM-3100V). Tapping-mode measurements were performed in air within a scan area of 20 × 20 µm². The macroscopic defects of the films were observed by confocal laser scanning microscopy (CLSM; VK-X200K).

The cross-sectional and surface FE-SEM images of the double-layer porous Si before and after mesoplasma annealing are shown in Fig. 1. The as-etched porous Si shows a spongy structure of the low-porosity layer on top of a dendritic structure of the high-porosity layer with columnar pores substantially perpendicular to the surface [Fig. 1(a)]. The surface of the low-porosity layer has small voids due to anode etching [Fig. 1(c)]. After being exposed to Ar–H2 mesoplasma for 42 s from 2 to 18 kW, as can be seen from Fig. 1(b), the structures of the porous Si layers changed completely: the columnar pores reorganized such that the high-porosity layer became a large extended void interrupted by a few pillars, whereas the low-porosity layer transformed into spheroidal voids embedded in a Si matrix. This structure is basically similar to that obtained by conventional annealing at H2 ambient for 30 min at 1050 °C.6,9) Moreover, note that the void size decreases with depth, i.e., the voids closer to the high-porosity layer are much smaller than those on top. This is consistent with that shown in Ref. 5. Therefore, the annealing process under the mesoplasma condition is reasonably considered to follow the classical sintering theory.22,23) It can also be understood, as has been reported in the reference, that porous Si reorganization occurs through vacancy diffusion processes driven by a vacancy concentration gradient between the pore (or voids) and its surrounding lattice.5) However, unlike the conventional process that forms a smooth surface free of open voids,6,24) the porous Si after Ar–H2 mesoplasma annealing shows a rough surface with large voids, as shown in Fig. 1(d). This phenomenon is considered to be due to H etching, because a large amount of atomic H is obtained under the mesoplasma condition and H atoms have a significant etching effect on Si.16,18,19) In fact, the etching of the porous Si by H atoms can be evidenced from Figs. 1(e) and 1(f), that is, there are no obvious etching pores observed after Ar plasma exposure [Fig. 1(e)], and similar etching pores are observed after the Ar–H2 plasma exposure of the Si wafer [Fig. 1(f)] under identical experimental conditions. The open voids on the porous Si are larger than those on the Si wafer, probably because the etching of the porous Si is more serious than that of the Si wafer.

The evolution of porous Si structures caused by Ar–H2 mesoplasma annealing is also indicated by normalized Raman scattering spectroscopy (Fig. 2). For comparison, the Raman spectrum of the monocrystal Si wafer is also shown in the figure. For the as-etched porous Si, the peak of the Raman spectrum is located at 519.6 cm⁻¹, which is lower

![Fig. 1. Cross-sectional FE-SEM images of the (a) as-etched double-layer porous Si and (b) double-layer porous Si after Ar–H2 mesoplasma annealing. Surface FE-SEM images of the (c) as-etched double-layer porous Si, (d) double-layer porous Si after Ar–H2 mesoplasma annealing, (e) double-layer porous Si after Ar mesoplasma annealing, and (f) Si wafer after Ar–H2 mesoplasma annealing.](image)

![Fig. 2. Raman spectra of the porous Si before and after Ar–H2 plasma annealing. The spectrum of the Si wafer is added for comparison (PSi: porous Si).](image)
than that for the monocrystal Si wafer at 520.7 cm$^{-1}$. This shift of the peak position is due to lattice expansion by anode etching,\(^{25,26}\) corresponding to a tensile stress in the film. After being exposed to the Ar–H$_2$ mesoplasma for 42 s from 2 to 18 kW, the Raman peak of porous Si shifts to a high wave number and the spectrum is almost coincident with that for the monocrystal Si wafer. This change in the peak position is due to the reorganization of the porous structure and the relaxation of the lattice expansion during annealing.\(^{27}\) The coincident Raman spectra indicate the low tensile stress of the annealed porous Si by mesoplasma under the current condition.

This significant annealing effect on porous Si by mesoplasma, in fact, can be obtained even at a shorter time under a high-power condition. In order to control the plasma exposure time, a BN plate shutter was set between the plasma torch and the substrate so that the exposure time can be controlled by opening and closing the shutter. The surface and cross-sectional FE-SEM images of porous Si annealed at 5, 8, and 15 s using Ar–H$_2$ plasma at 18 kW are shown in Figs. 3(a) and 3(b), respectively. The surface and cross-sectional FE-SEM images of porous Si annealed at 5 s, 8 s, and 15 s using Ar–H$_2$ plasma at 18 kW are shown in Figs. 3. It is seen that all of the porous Si films subjected to a short-time mesoplasma exposure exhibit an obvious annealing phenomenon, i.e., the high-porosity layer becomes a large extended void, whereas the low-porosity layer transforms into spheroidal voids embedded in a Si matrix. It is also seen from the figure that the spheroidal voids in the low-porosity layer become more significant with increasing exposure time, corresponding to the increased annealing effect on porous Si. However, the surface of the low-porosity layers becomes rougher: the size of the open voids increases from 30–80 to 300–1000 nm and the surface roughness increases from 7.8 to 126.6 nm by increasing the exposure time from 5 to 15 s. This increase in the surface roughness is primarily due to the increased H-etching effect by increasing the exposure time. Therefore, a few seconds of exposure to mesoplasma under a high-power condition has a significant annealing effect, similar to that of conventional H$_2$ annealing for a long time of 30–60 min; an increase in the annealing time with mesoplasma exposure is not necessarily good because the surface of the porous Si becomes rougher owing to H etching. Note that the substrate temperature is measured to be about 800–900 °C; this significant annealing effect by such a short-time annealing at this temperature range may not be understood on the basis of the classical sintering theory. One of the possible reasons could be that the temperature on the very top of the surface is very high owing to the direct exposure to the high-temperature plasma, which cannot be measured in our current facility. The details of the annealing effect by mesoplasma are under investigation.

The surface and cross-sectional FE-SEM images of the Si film deposited on the annealed porous Si (42 s annealing from 2 to 18 kW) are shown in Figs. 4(a) and 4(b), respectively. Those of the Si film deposited on a polished Si wafer [Figs. 4(c) and 4(d), respectively] under identical experimental conditions are also shown in the figure for comparison. It is seen that the Si film deposited on the annealed porous Si by MPCVD shows a uniform surface with no obvious grains [Fig. 4(a)], which is similar to that deposited on the polished Si wafer [Fig. 4(c)]. Although a clear interface layer is observed from the cross-sectional FE-SEM image of the as-cleaved Si film deposited on the porous Si [Fig. 4(b)], i.e., the annealed porous layer with a few pillars in a high-porosity layer interconnecting a low-porosity layer to the substrate, there is no obvious interface between the Si film and the low-porosity layer, as shown in Fig. 4(e) (the dashed line in the figure indicates the possible position of the film–substrate interface according to the thickness of the porous Si layer). The cross-sectional FE-SEM image also shows a plain structure of ~13 µm thickness for the Si film deposited on porous Si, corresponding to a deposition rate of
350 nm/s. This plain structure is also similar to that deposited on a polished Si wafer [Fig. 4(d)]. The XRD patterns (not shown here) exhibit only a Si(400) peak for the films deposited on both the porous Si and the Si wafer, which has the same orientation as that of the (100)-oriented monocrystalline Si substrate. This indicates the epitaxial feature of the films, as has been confirmed from the transmission electron microscopy (TEM) observation of the films with such XRD patterns.11) The single crystalline structure of the film deposited on the porous Si is also confirmed from the EBSD result, as shown in Fig. 4(f), that is, the film has a uniform orientation of [001] in an area of 13 × 13 μm². Although the surfaces of the Si films deposited on both the annealed porous Si and the polished Si wafer are flat, as revealed by FE-SEM, they show anisotropic square defects from the surface, as revealed by CLSM. These defects are suggested to be due to the stacking fault originating from the initial growth surface, i.e., the substrate surface, as reported in Refs. 19 and 28. The root-mean-square (RMS) roughness and defect density of the films were investigated at three and ten arbitrary positions, respectively, and the results are shown in Fig. 5. It is seen that the RMS roughness of the film deposited on the annealed porous Si is 3.1 ± 0.2 nm, which is similar to that of the film deposited on the Si wafer (3.6 ± 0.8 nm). The defect density of the film deposited on the annealed porous Si is (2.6 ± 0.1) × 10² cm⁻²; this is also similar to that of the film deposited on the Si wafer [(2.0 ± 0.6) × 10³ cm⁻²]. Therefore, even if the surface of the porous Si after Ar–H₂ mesoplasma annealing is rough with large open voids, the Si films deposited on such a substrate by MPCVD showed a smooth and plain structure, similar to that of the films deposited on a polished Si wafer. This is quite different from that obtained by the conventional process where a smooth surface is required to obtain films with a low defect density and a smooth surface.24) The above-mentioned phenomenon demonstrates the advantages of the cluster-assisted mesoplasma process where film deposition is based on the formation of loosely bonded nanoclusters, and the simultaneous and instantaneous rearrangements of the Si atoms on the substrate surface contribute to epitaxial Si film growth.

To conclude, we have investigated in situ annealing and epitaxial silicon film growth on porous silicon by the mesoplasma process. Annealing for a few seconds using Ar–H₂ mesoplasma results in a porous Si structure similar to that obtained by conventional H₂ thermal annealing for more than 30 min. Although the surface of the annealed porous Si is rough primarily owing to atomic hydrogen etching, the epitaxial Si films deposited at a rate of 350 nm/s using Ar–H₂–SiH₄ mesoplasma exhibit properties identical to those of the films obtained on a polished Si wafer. These could be another advantage of cluster-assisted mesoplasma chemical vapor deposition compared with conventional processes.

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