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Effect of hydrogen plasma precleaning on the removal of interfacial amorphous layer in the chemical vapor deposition of microcrystalline silicon films on silicon oxide surface

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Microcrystalline silicon(μc-Si) film deposited on silicon oxide in a remote plasma enhanced chemical vapor deposition (RPECVD) with disilane (Si_2H_6) and silicon tetrafluoride (SiF_4) has been investigated. It was found that *in situ* hydrogen plasma cleaning of the substrate prior to deposition is effective to reduce the interfacial amorphous transition region. It is believed that hydrogen plasma cleaning generated adsorption and nucleation sites by breaking weak Si–O and Si–Si bonds and also removed oxygen/carbon impurity. Surface roughening was observed from the hydrogen plasma precleaning which helped nucleation and crystallization at the initial stage of the growth. © *1996 American Institute of Physics.* [S0003-6951(96)01016-3]

Recently, microcrystalline silicon films (μc-Si) have been used for thin-film transistors (TFTs) in the field of active matrix liquid crystal displays (AMLCDs). The use of crystalline silicon as an active layer instead of amorphous silicon has drawn much attention because its electron mobility is much higher than that of *a*-Si and better performance can be achieved with poly-Si TFT.[1–3] In AMLCD application, low-temperature processing below 600 °C is desirable to reduce the manufacturing cost by utilizing low cost glass substrate. However, it is relatively difficult to grow crystalline films because adatom mobility is low and incorporation of impurities, especially oxygen is more likely.

In situ plasma cleaning prior to silicon epitaxy has been studied to remove remaining surface contaminants such as oxygen and carbon from single-crystal silicon substrate surface at low temperatures (<600 °C). Various sources such as radio frequency remote plasma[4–6] and electron cyclotron resonance (ECR)[7–11] plasma excited argon, helium, and hydrogen have been reported. Hydrogen plasma cleaning is from a chemical etching by hydrogen atoms and ions and it has been used as a substitute for inert (Ar and He) plasma cleaning to avoid physical damage.[9,11]

Semiconductor active layers in thin-film transistor applications are usually grown on a substrate which is not crystalline. The effects of surface roughness and contamination of amorphous substrate on the growth and microstructure of the active layer are not fully understood. It has been thought that the surface roughness may affect the diffusion of the deposition precursor and relaxation of the Si network during film growth.[12]

In this research, microcrystalline silicon film deposited on silicon oxide in a remote plasma enhanced chemical vapor deposition (RPECVD) with disilane (Si_2H_6) and silicon tetrafluoride (SiF_4) has been investigated. We have investigated the effect of *in situ* hydrogen plasma cleaning of the SiO_2 substrate on the initial nucleation and crystal growth. We added SiF_4 because it is generally known that oxygen and other impurity incorporation can be reduced from *in situ* chemical cleaning effects of fluorine and crystalline phase can be grown at low temperatures.[13,14]

In a remote plasma enhanced CVD reactor, hydrogen (H_2) is introduced into an alumina tube and excited by inductively coupled rf (13.56 MHz) plasma and flown into the deposition zone. This plasma is used for the SiO_2 substrate precleaning. For deposition, disilane (Si_2H_6) and silicon tetrafluoride (SiF_4) are introduced into the region 10 cm downstream of the plasma. These reactant gases are mixed with excited hydrogen and flown toward the substrate 20 cm downstream of the plasma. Thermally oxidized 4 in. silicon wafers with an oxide thickness of 100 mm were used as substrates. For *in situ* hydrogen plasma cleaning, the pressure was 0.3 Torr, temperature was 300 °C, plasma power and hydrogen flow rate were 100 W and 100 sccm, respectively. On the other hand, for μc-Si deposition, reactor pressure was 0.4 Torr, deposition temperature was 430 °C, plasma power and SiF_4 flow rates were 60 W and 0–30 sccm, respectively. The deposition rate was in the range of 3–10 nm/min.

The surface roughness of SiO_2 substrate and deposited Si film was observed using atomic force microscopy (AFM). The root-mean-square (rms) value of surface roughness was obtained by averaging ten different areas. The interfacial composition was examined by Auger electron spectroscopy (AES) at a voltage of 3.5 keV. To observe the microstructure of the silicon film on SiO_2, transmission electron microscopy (TEM) was used. Cross-sectional specimens for TEM were first glued face to face, cut, then ground, dimpled, and thinned by ion milling. TEM observations were conducted using a transmission electron microscopy operating at 100 kV.

We have performed *in situ* hydrogen plasma cleaning and investigated the surface roughness of the substrate surface. AFM images in Fig. 1 show the surface roughening as a function of *in situ* hydrogen plasma cleaning time. The rms value of surface roughness of thermal oxide is 0.2–0.49 nm without any treatment. The rms of oxide surface is increased to 1.65 nm for 10 min and 2.2 nm for 30 min hydrogen plasma cleaning, respectively. The creation of free-surface

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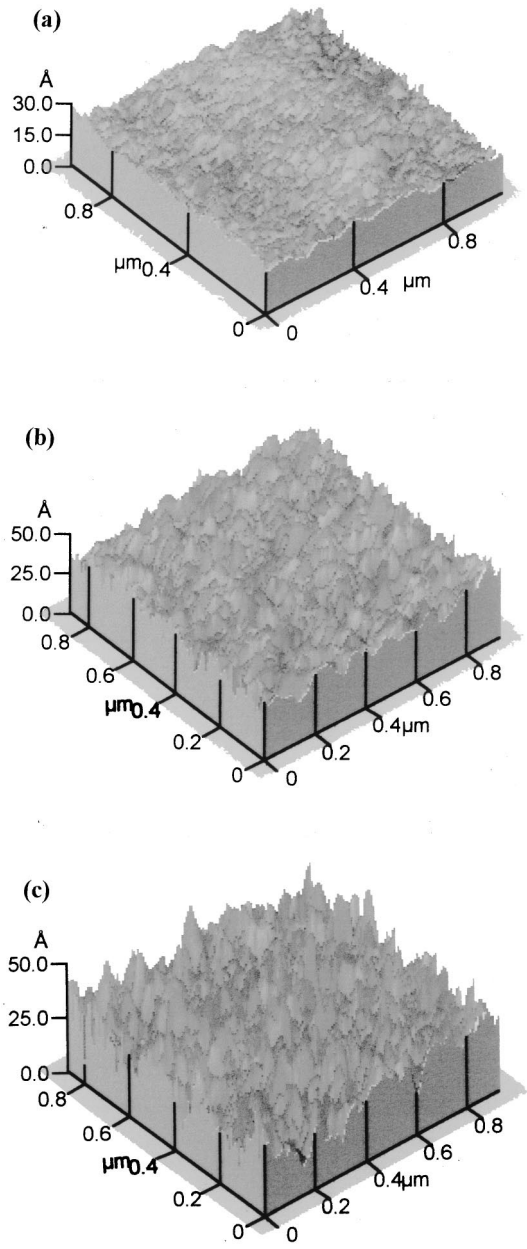

FIG. 1. Three-dimensional AFM images of the SiO_2 substrate with hydrogen plasma cleaning for (a) 0, (b) 10, and (c) 30 min. Plasma power at 100 W, substrate temperature at 300 °C, and pressure at 0.3 Torr.

area and roughness on the initial growing surface was due to the inhomogeneous etching by hydrogen plasma. Hydrogen radicals preferentially remove weak Si–Si bond and break Si–O bond at the top of the SiO_2 surface to create voids and dangling bonds.

Silicon atoms arriving at roughened surface easily adhere to the surface sites and are immediately trapped by voids and dangling bonds on the SiO_2 surface. In fact, *in situ* hydrogen plasma cleaning prior to deposition increased the deposition rate by more than 15%. It is also expected that plasma cleaning will help the film growth with crystalline character from the early stage of film growth.

Figure 2 shows cross-sectional TEM images. Without *in situ* hydrogen plasma cleaning [Fig. 2(a)], the interface region of deposited-Si film on amorphous SiO_2 does not show

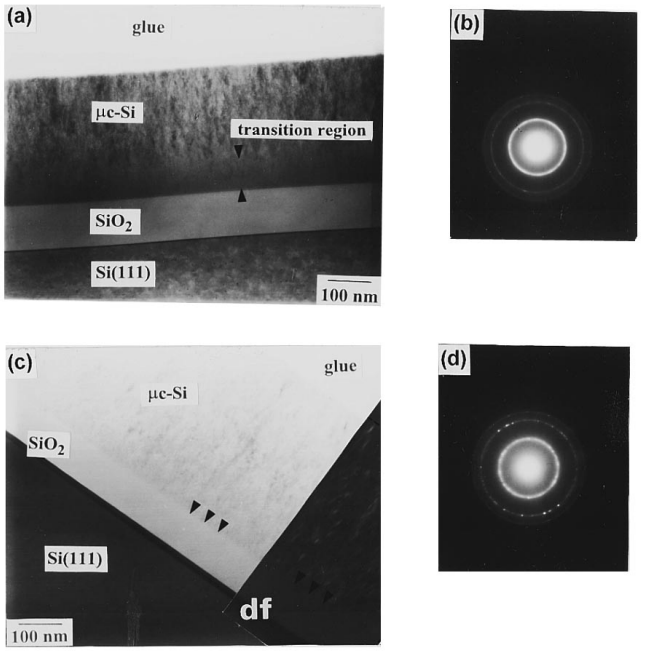

FIG. 2. Cross-sectional TEM images and their selective area diffraction (SAD) pattern of Si films deposited with $Si_2H_6/SiF_4/H_2=0.1/30/100$ at a temperature of 430 °C, pressure of 0.4 Torr and plasma power of 60 W. (a) Bright field image without hydrogen plasma cleaning, (b) SAD for (a), (c) bright field and dark field image with hydrogen plasma cleaning for 5 min and (d) SAD for (c).

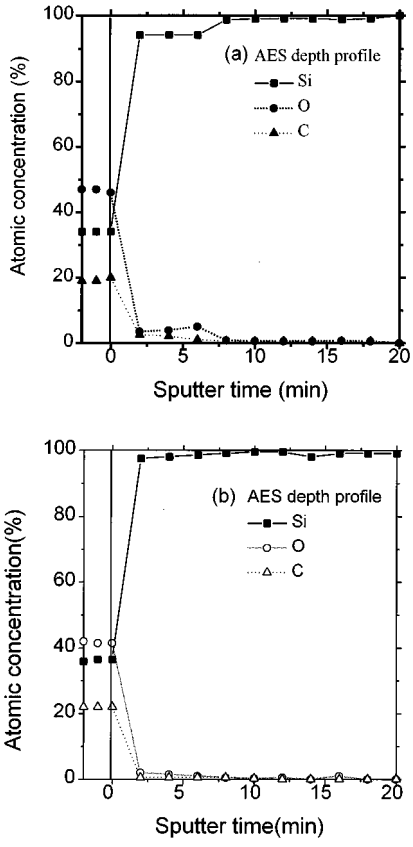

FIG. 3. AES depth profile (a) without and (b) with hydrogen plasma cleaning. Plasma power at 100 W, temperature at 300 °C, pressure at 0.3 Torr and plasma cleaning for 5 min.

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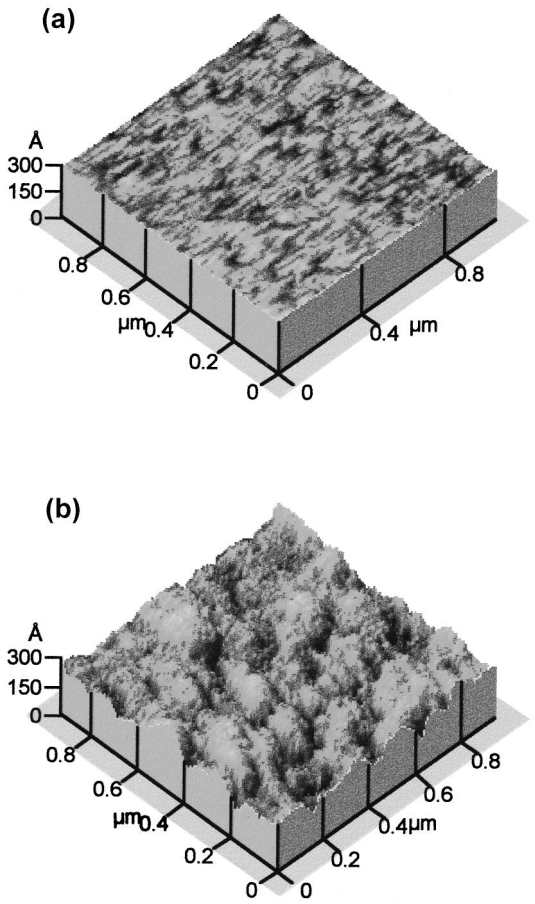

FIG. 4. Three-dimensional AFM images of Si surface roughness. The scan range is 1 μm×1 μm. Si_2H_6/H_2=0.1/100, temperature at 430 °C, plasma power at 60 W (a) without SiF_4 and (b) with SiF_4 addition at 30 sccm.

crystalline phase and the transition layer thickness is about 70 nm as marked with arrows in Fig. 2(a). Formation of this transition region could be suppressed with *in situ* plasma cleaning as shown in Fig. 2(c) with arrows. This shows that hydrogen plasma cleaning on the initial surface strongly affected the crystallization processes. The silicon film deposited with SiF_4 exhibits a columnar structure growing in a direction perpendicular to the substrate. The concentric circles of the selected area diffraction (SAD) patterns [Figs. 2(b) and 2(d)] indicate that the silicon film deposited with SiF_4 is polycrystalline. By XRD and TEM results, both silicon films were found to have a preferred orientation along the growth direction with the ⟨110⟩ of the film parallel to the ⟨111⟩ of the substrate. The film was found to be made up of very small needle-like grains ~4 nm in width and 20 nm in length from the dark field image [df in Fig. 2(c)], and those are uniformly distributed in the thickness of the film.

Figure 3 shows AES depth profiles before and after hydrogen plasma cleaning. A single-crystal silicon wafer was used because the cleaning effect can be detected more easily on this native oxides. One of the obstacles disturbing the growth of crystalline Si films at low temperature is the impurities (especially oxygen and carbon) remaining in a non-UHV vacuum chamber which cover and react immediately with the surface of growing silicon.[16] After hydrogen plasma cleaning oxygen as well as carbon was detected below the 1 at. % level. It means that the atomic hydrogen reacted with surface impurities and reaction products were desorbed as a form of volatile hydrides. It shows that hydrogen plasma cleaning is effective in removal of impurities.

Figure 4 shows AFM images of silicon films deposited with or without SiF_4 addition and with *in situ* hydrogen plasma precleaning. Without SiF_4 addition, the Si surface is relatively smooth and the surface roughness of SiO_2 after the precleaning is not preserved. This film was confirmed to be amorphous.[15] On the other hand, with SiF_4 addition, rugged mountains with a larger diameter than precleaned oxide surface were observed. From the combined results of TEM and AFM, the average diameter of the rugged mountains obtained from AFM does not coincide with real grain size. Because μc-Si films have very small grain size from 2 to 20 nm and are mixed with both crystalline and amorphous phases, it seems that apparent grains obtained by AFM are coagglomerated small grains.

In summary, we have deposited the μc-Si films on SiO_2 substrates and investigated the effect of *in situ* hydrogen plasma precleaning. *In situ* hydrogen plasma is effective in removing oxygen and carbon impurities and also induces surface roughening which gives favorable adsorption sites for crystalline film growth. Although SiF_4 addition roughened the deposited-film surface, crystalline silicon films with ⟨110⟩ preferential orientation could be obtained with appropriate amounts of SiF_4.

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