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Effect of surface roughness on the quality of silicon epitaxial film grown after UV-irradiated gas phase cleaning

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Abstract In-situ cleaning and subsequent silicon epitaxial film growth were performed in a load-locked reactor equipped with Hg-grid UV lamp and PBN heater to obtain the smooth and contaminant-free underlying surface and develop low-temperature epitaxial film growth process. The removals of organic and native oxide were investigated using UV-excited O_2 and NF_3/H_2, and the effect of the surface condition was examined on the quality of silicon epitaxial film grown at temperature as low as 750°C. UV-excited gas phase cleaning was found to be effective in removing the organic and native oxide successfully providing a smooth surface with RMS roughness of 0.5 Å at optimal condition. Crystalline quality of epitaxial film was determined by smoothness of cleaned surface and the presence of native oxide and impurity. Crystalline defects such as dislocation loops or voids due to the surface roughness were observed by XTEM.

1. Introduction

Epitaxial growth of silicon is one of the potential technologies for ultra-large-scale-integrated (ULSI) devices. The key requirement for the successful silicon epitaxy for ULSI is to achieve the contaminant-free silicon surfaces with atomic-level smoothness before growth while maintaining a thermal budget compatible with dopant diffusion requirements. Surface cleaning has been known to influence the structure of silicon epitaxial films and the success of low-temperature growth processes. Various methods have been investigated for *in situ* cleaning prior to silicon epitaxial growth. These cleaning methods include thermally assisted cleaning [1], photo assisted cleaning [2], plasma assisted cleaning[3-6], and HF vapor cleaning [7].

Problem of conventional thermal process for native oxide removal is that it cannot desorb the residual carbon contaminant and SiC precipitates, the origin of strain in the epitaxial film, are formed. Under the critical condition occurred in the high temperature treatments, the induced strain relaxes via the formation of dislocations, which are fatal defects for devices.

On the other hand, the quality of deposited epitaxial film is directly related to the roughness of underlying surface such that rough surface yields heavily twinned epitaxial film [3]. Therefore surface smoothness is indispensable to the successful epitaxial film growth. The quality of deposited epitaxial film is directly related to the roughness of underlying surface. The surface roughness can be controlled by the surface cleaning process prior to the growth.

In this work, in-situ cleaning and subsequent silicon epitaxial film growth were performed in a load-locked reactor equipped with Hg-grid UV lamp (BHK Inc.) and PBN (pyrolytic boron nitride) heater to obtain smooth and contaminant-free underlying surface and develop low temperature-epitaxial film growth process. The removal of organic and native oxide were investigated using UV-excited O_2 and NF_3/H_2 and the effect of the surface condition was examined on the quality of silicon epitaxial film grown at temperature as low as 750°C. Fourier transform infrared spectrometer (FT-IR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used to characterize the cleaned surface for the surface roughness and chemistry of organic and native oxide. Cross-section transmission electron microscopy (XTEM) was used to investigate the deposited silicon epitaxial film for the crystalline quality and to correlate it with the surface roughness which formed as a result of UV-NF_3/H_2 cleaning for native oxide removal as a function of composition.

2. Experiment

For the sample preparation, thermal silicon oxide of

180 nm thick film was grown on a 4-inch, p-type (100) oriented wafer (R_S = 22 - 38 Ω-cm) by wet oxidation at 950°C in the furnace. Native (chemical) oxide was grown on the same kind of wafer as for thermal oxide after cleaning with acetone-ethanol-deionized water in sonicating bath and drying with nitrogen blowing. Thin poly ethylene glycol film was coated by spin coating after pre-cleaning. The samples were cut into the pieces of 2 cm×2 cm and mounted on the sample holder. The cleaning experiments were carried out in a load-locked cleaning reactor equipped with a UV lamp in the reactor for the exposure to reaction gas and substrate. Prior to UV-excited NF_3/H_2 cleaning for oxide removal, the wafer was treated in a UV-excited oxygen cleaning for 15 min to remove hydrocarbon molecules from the surface. Reactor chamber pressure, oxygen flow rate and UV lamp power as a process parameter were studied for PEG removal with UV power of 4~5 mW/cm^2 in the distance of 2.54 cm at the wavelength of 185 nm. Then, UV-excited NF_3/H_2 gas phase cleaning experiments were carried out in the same chamber. Total flow rate, the distance between the wafer and the UV lamp, and cleaning time were fixed at 20 sccm, 3.5 cm and 30 minute, respectively. During the gas cleaning, substrate was heated from room temperature to about 70°C by UV irradiation. Chamber pressure and UV lamp power conditions are the same as for UV/O_2 cleaning. For the deposition of silicon epitaxial film, samples were heated from 20°C to 750°C in 5 min. H_2 and SiH_4 flow rates (50 sccm and 0.5 sccm, respectively) as well as the process pressure (200 mTorr) were established prior to heating.

Mass spectrometer (VG SX-200) was used to detect the gas phase species at various etching gas compositions. Probe position for the sampling was fixed at the height of 2 mm above the sample surface for more effective sampling of by-product species. The sampling stream from the reactor chamber was sent to mass spectrometer and 1/16 in stainless steel tube was used as a probe tip to minimize the effect of depletion of reactive species above the surface at the cost of missing by-product species with short life time and time lag. Schematic of UV irradiated GPC reactor was shown in Fig. 1. We also examined the removal characteristics of native oxide after gas cleaning by XPS (Specs, LHS10). Roughness of the surface was measured using AFM (PSI). TEM images and diffraction patterns were obtained to determine the quality of the interface and crystalline quality of deposited Si film.

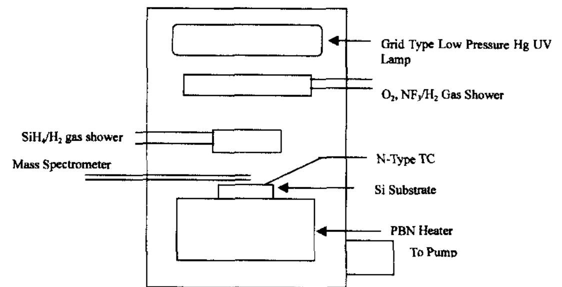

Fig. 1. Schematic Diagram of UV-GPC Reactor.

3. Results and discussion

To examine the growth of native oxide after wet cleaning, sample wafer was cleaned with acetone (3 min)-ethanol (3 min)-HF (5 %) (30 sec.) with deionized water rinse (3 min) after each step and was dried

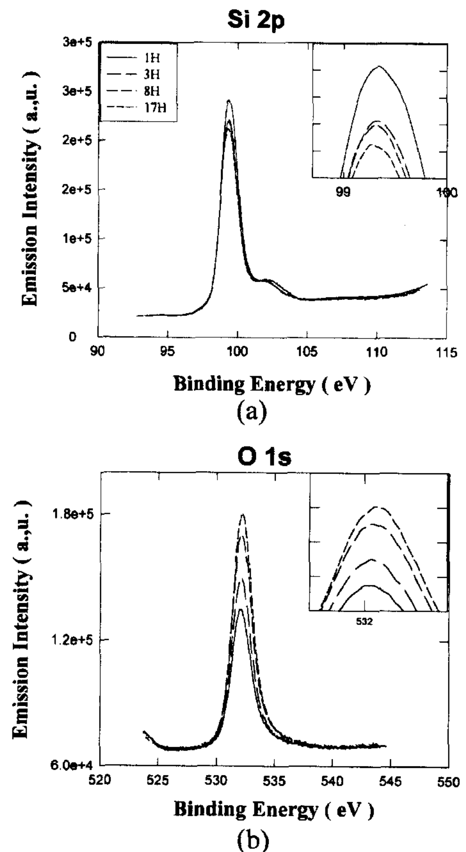

Fig. 2. XPS spectra of (a) Si2p and (b) O1s of silicon surface as a function of exposure time in air after dipping in HF (50 : 1) for 30 sec. (Exposure time in air : 1, 3, 8, 17 Hour).

tion of exposure time in air are shown in Fig. 2. After short time exposure in air, the existence of native oxide was confirmed in XPS spectra. Native oxide was grown further fast as the sample was exposed in air. This suggests that the removal of native oxide by HF wet cleaning is not complete to prevent the regrowth of native oxide.

The combination of UV excited O_2 and direct exposure on organic material such as poly ethylene glycol on silicon wafer was used to investigate the removal of carbon contaminants and the effect of processing variables such as substrate temperature, process time, and pressure. Figure 3 shows infrared absorption spectra of C - O, C = O, and CH_3 of the spin coated PEG (poly-ethylene glycol) film taken (a) after as-coating, (b) after UV/O_2 cleaning and (c) after O_2 cleaning. The bare wafer was used as the background reference spectra. Figure 3 (a) is a reference spectra of PEG. Figure 3 (b) and 3 (c) show effect of UV irradiation for PEG removal using O_2 as a reactive reagent. Compared to PEG, the intensity of the band around 1740 cm^{-1} due to > C = O increased and that around 2870 cm^{-1} due to > CH decreased in the sample after just O_2 cleaning. This means that PEG can be oxidized by O_2 without UV irradiation. But removal rate is lower than the case of with UV irradiation. From this we can see that UV irradiation excites oxygen to produce ozone and atomic oxygen which react with PEG more easily. The removal rate of PEG with UV/O_2 was more than 36 nm/min. Figure 4 shows FTIR absorption spectra of poly ethylene glycol after exposure to UV/O_2 as a function of pressure, process time and substrate temperature. Since the spectrum was obtained using as-coated samples spectra as reference, growing of the negative peaks at 2870 cm^{-1} represents a decrease of the C-H species on the surface. Figure 4 (a) shows that the etch rate increased with pressure

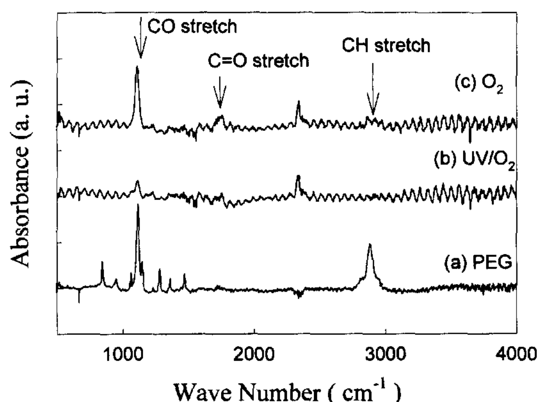

Fig. 3. FTIR absorption spectra of C - O, C = O, and CH_3 of the spin coated PEG (poly-ethylene glycol) film taken (a) after as-coated, (b) after UV/ O_2 cleaning and (c) after O_2 only cleaning. (*Coating condition* : PEG (2 wt% in acetonitrile), rpm = 1770, time = 3 min, 1'st curing (60°C, 30 min), 2'nd curing (100°C, 30 min), *Cleaning Condition* : Pressure = 5 Torr, Temp. = 200°C, Time = 150 sec., O_2 flow rate = 50 sccm).

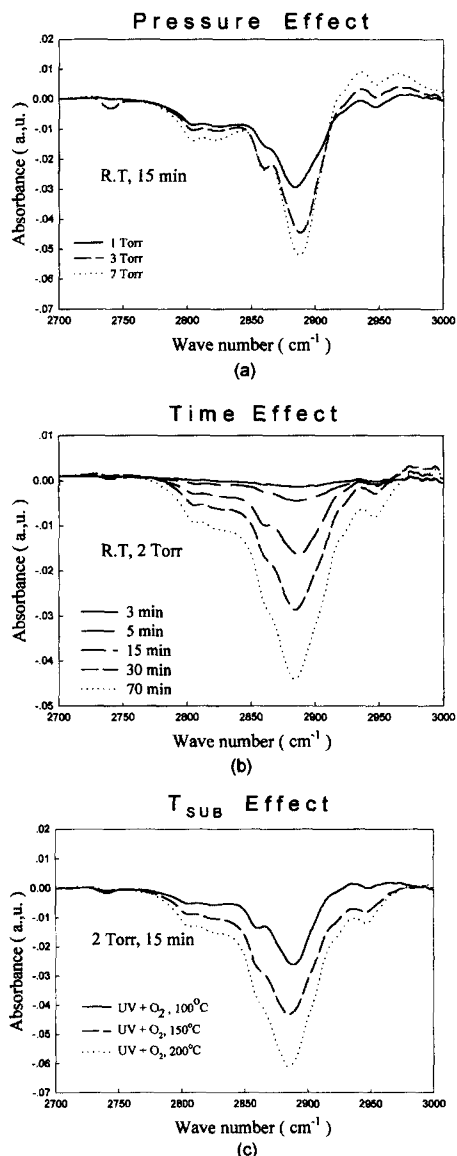

Fig. 4. FTIR absorption spectra after UV excited O_2 exposure of poly ethylene glycol as a function of process pressure, time and substrate temperature.

but its increase rate decrease with pressure. It is because exciting rate by UV irradiation is low and quenching rate by bombardment between excited molecules and cold molecules is high in this pressure range. Figure 4 (b) shows that the etch rate increased linearly with time. Figure 4 (c) shows the large effect of substrate temperature on the etch rate with UV/O_2. Ozone can be thermally decomposed to molecular oxygen and atomic oxygen [8]. The atomic oxygen produced via photochemical or thermal dissociation of O_3 is believed to be the predominant etchant species and organic materials are broken into simple volatile products such as CO_2, H_2O, etc over the temperature range of 100~300°C. Thus, higher temperature enables the faster removal of organics. But increase of temperature is limited by diffusion of metallic contaminants into silicon bulk. Organic removal condition for UV excited O_2 GPC was fixed at 15 min, 2 Torr, and R.T for minimum native oxide growth. At this condition, perfect removal of organic contaminants was confirmed by successful growth of epitaxial film on that surface.

XPS spectra of Si 2p and O 1s obtained from a processed sample in Fig. 5 show the effective removal of native oxide by UV-excited NF_3/H_2 gas cleaning. Weak intensity of O 1s and Si 2p obtained from processed wafer is thought to be caused by air exposure during transportation to analyzer chamber. F 1s peak is actually a convolution of two peaks. One of the peaks is associated with a weakly bound state of fluorine, while the other peak is due to a strongly bound chemisorbed state of fluorine. F 1s peak at 687.6 eV of processed wafer is associated with a weakly bound state and that of thermal oxide is associated with a strongly bound state of fluorine. The intensity of F 1s peak and the degree of hydrogen termination mainly depend on process conditions, density of step edges and composition of H_2/NF_3 in reacting gas.

Figure 6 shows that etch rate of SiO_2 and Si in the $UV/NF_3/H_2$ etching gas system as a function of H_2 composition in the feed gas at the pressure of 2 Torr and flow rate of 20 sccm. Etch rate of SiO_2/Si was indirectly obtained by measuring the SiF_3 partial pressure by mass spectrometer. Although the etch rates of thermal oxide and silicon decreased with the increasing ratio of H_2/NF_3 flow rate, the etch selectivity of SiO_2/Si increased to 1.8. With native oxide we expect higher etch selectivity of SiO_2/Si since native oxide is known to be etched much easier than thermal oxide [9].

Partial pressure variation of H and HF was mea-

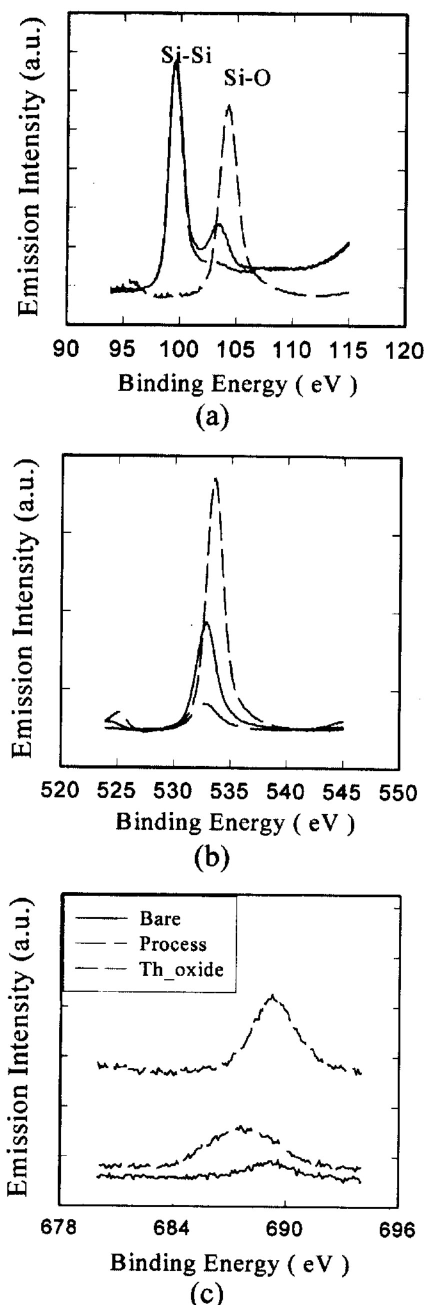

Fig. 5. XPS spectra of (a) Si2p, (b) O1s and (c) F1s peaks on a bare wafer, a processed wafer, and a wafer with thermal oxide (pressure = 2 Torr, NF_3/H_2 flow rate = 10/10 sccm).

sured by mass spectrometer as a function of H_2 flow rate during oxide etching. Partial pressure of F was expected to decrease with the increase of the ratio of

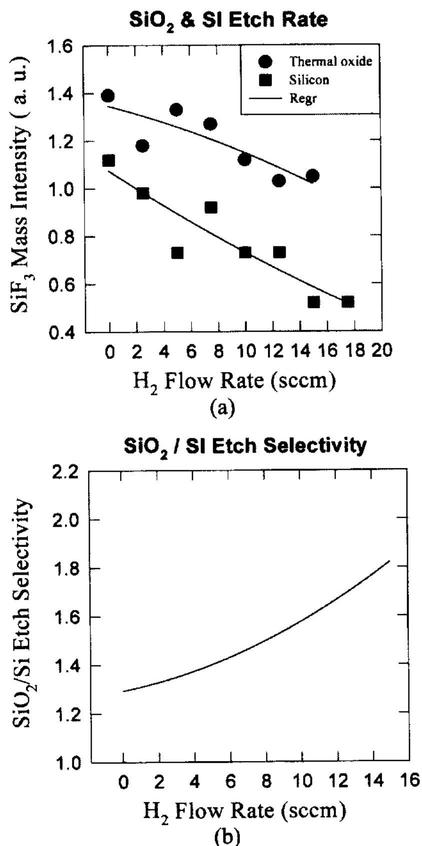

Fig. 6. Etch rate of SiO_2 and Si in a NF_3/H_2 etching gas system as a function of H_2 proportion in feed gas with UV irradiation (Process condition : Pressure = 2 Torr, Total flow rate = 20 sccm).

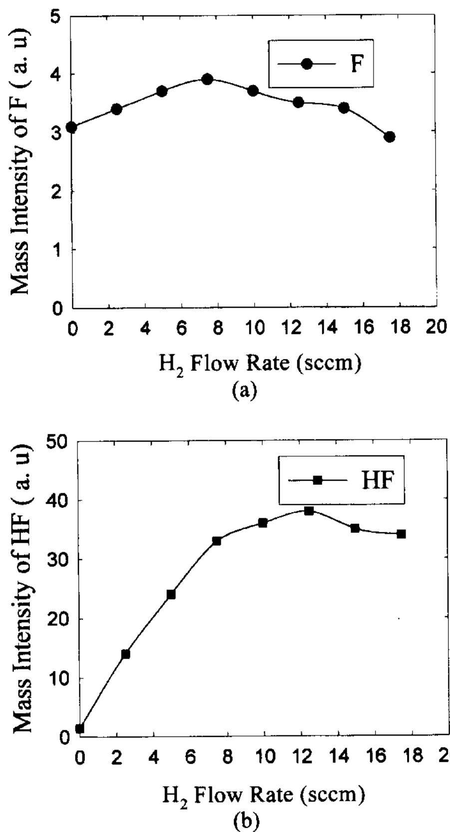

Fig. 7. (a) F and (b) HF partial pressure variation measured by mass spectrometer as a function of H_2 flow rate during oxide etching. (total flow rate = 20 sccm, pressure = 2 Torr).

H_2/NF_3 flow rate. In Fig. 7, however, it did not decrease as much as expected. Partial pressure of HF increased with H_2 flow rate and shows maximum at the flow rate ratio of about 1 (H_2 flow rate = 10 sccm), as expected. The reason why the partial pressure of F did not decrease as much as expected can be speculated as the cracking of HF in the mass spectrometer.

RMS roughness of processed wafer surface was measured by AFM and shown in Fig. 8 as a function of H_2 flow rate. The RMS roughness on silicon surface after gas phase cleaning can be divided into three regimes by H_2 contents in gas mixture, RMS roughness and surface topography. Corresponding AFM image in each regime are shown together. The etching of native oxides in UV-excited NF_3 gas causes pitting on silicon surface through excessive etching of silicon by fluorine. Hydrogen scavenges fluorine to form HF and prevents excessive etching of silicon [9]. Silicon

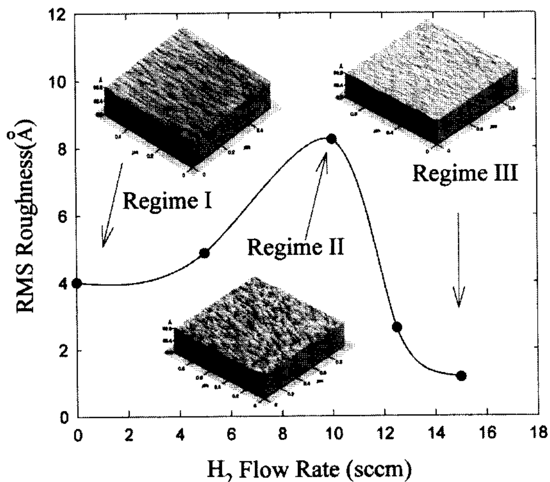

Fig. 8. RMS roughness and AFM surface images of processed wafer surfaces as a function of H_2 flow rate. (pressure = 2.0 Torr, total flow rate = 20 sccm).

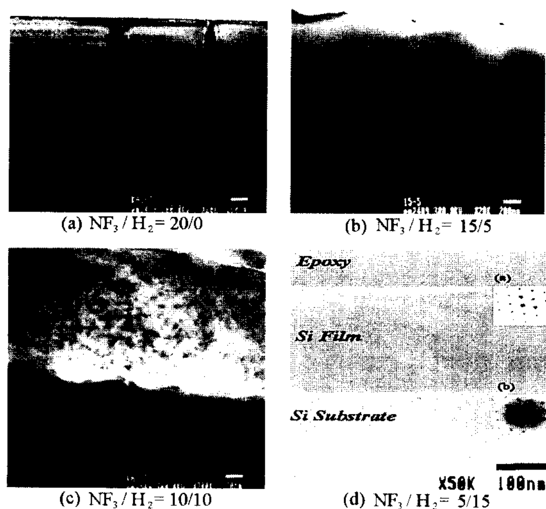

Fig. 9. TEM images of deposited Si film on pre-cleaned silicon surface as a function of NF_3/H_2 composition. (Silicon epitaxial film growth condition : SiH_4 flow rate = 0.5 sccm, H_2 flow rate = 50 sccm, Pressure = 200 mTorr, Substrate Temperature = 750°C).

surface pitting was not observed when content of H_2 in the etching gas mixture was 75 % or higher, where RMS surface roughness was measured as 0.5 Å.

We have taken the XTEM image of silicon epitaxial film grown after NF_3/H_2 gas phase cleaning. Figure 9 (a)-(c) show that a number of large dislocation loop, voids and interfacial defects in silicon film grown by low temperature CVD was induced by pits and roughness of cleaned surface. Figure 9 (d) shows that interfacial smoothness is very good because oxide removal was carried out under conditions corresponding to regime (III) in Fig. 8, where the oxide layer is considered to be completely removed. Diffraction pattern of epitaxial layer using SAD (selected area diffraction) technique confirmed crystallinity of deposited layer. SAD pattern of silicon epi-layer and substrate was inserted in Fig. 9 (d).

4. Conclusions

The removal of native oxide using HF wet etching could not be effective and native oxide regrowth in the atmosphere occurred rapidly. UV-excited gas phase cleaning was effective in removing the organic and native oxide successfully resulting in smooth surface with RMS roughness of 0.5 Å at optimal condition. Crystalline quality of epitaxial film was determined by smoothness of cleaned surface, the presence of native oxide and carbonaceous contaminants. Crystalline defects of deposited epitaxial film such as large dislocation loops and voids in film due to the surface defects were observed by XTEM.

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