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ArF excimer laser induced photolytic growth of Si homoepitaxial films from Si_2H_6 at 330 °C

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This letter discusses low-temperature Si homoepitaxy on Si(100) substrates by the photolytic decomposition of Si_2H_6 by the 193 nm emission of an ArF excimer laser. The chemical vapor deposition process at growth rates from 0.5–4 Å/min is performed in an ultrahigh vacuum chamber which, along with an *ex situ* HF dip and a novel *in situ* hydrogen clean using laser excitation, results in minimization of oxygen and carbon contamination which inhibits Si epitaxy. The growth involves photolytic decomposition of Si_2H_6 and the generation and adsorption of SiH_2 precursors on the hydrogenated Si surface, which is the rate limiting step. Very low defect density films in terms of stacking faults and dislocation loops (less than 10^6 cm^{-2}), and excellent crystallinity have been grown at 330 °C and 0.5 W laser power, as confirmed by Schimmel etching and Nomarski microscopy, transmission electron microscopy, electron diffraction and *in situ* reflection high-energy electron diffraction.

Low-temperature Si homoepitaxy to achieve ultrasharp doping transitions or heterointerfaces necessitates ultrahigh vacuum (UHV) processing, and nonthermal excitation such as plasma, photons, or energetic ions to dissociate the reactants and increase adatom mobility on the Si surface.[1] In this work, we have used photolysis of Si_2H_6 by an ArF excimer laser passing tangentially across the wafer surface to ensure that there is no laser-irradiation-induced damage or heating (with concomitant parallel pyrolytic processes) of the wafer surface to grow very low defect density Si homoepitaxial layers at temperatures as low as 330 °C in an UHV (3×10^{-9} Torr) system. Si_2H_6 is used instead of SiH_4 because SiH_4 has a very small absorption cross section of 2×10^{-22}–2×10^{-21} cm^{+2} even for deep ultraviolet excitation (190–200 nm).[2] Such highly selective, nonthermal dissociation of Si_2H_6 using the monochromatic 193 nm emission from the ArF laser can minimize parallel reaction pathways, thereby improving film morphology, and allow the growth of semiconductor devices with abrupt heterointerfaces and doping transitions.[3] Although Si photoepitaxy using Si_2H_6 has been achieved before, it has generally involved less selective, broad-band sources such as Hg lamps at higher temperatures (600 °C) in non-UHV system (1×10^{-6} Torr base pressure).[4] Work with ArF laser photolysis of Si_2H_6 has involved direct irradiation of the Si surface, possibly involving pyrolytic as well as photolytic mechanisms, as well as potential for surface damage.[5] Lower temperature photoepitaxy has been achieved at 200 °C, but with broadband sources and with UHV-incompatible gases such as SiH_2F_2.[6] Our approach is unique and has distinct advantages compared to previous techniques.

Silicon (100) lightly B-doped, 4″ substrates are solvent cleaned (trichloroethane, acetone, methanol, and de-ionized water), followed by a RCA clean and a dilute HF (40:1 dilution in de-ionized water) dip to remove the native oxide.[7] This also hydrogen passivates the surface, and makes it chemically inert to readsorption of oxygen and carbon. The oxygen coverage on such hydrogen-terminated Si(100) surfaces is about 0.01 monolayer, corresponding to about 3×10^{14} oxygen atoms over the area of the wafer covered by the laser beam.[8] The wafers have a polysilicon/oxide stack over a fourth of the wafer, which allows convenient measurement of the increase of the polysilicon thickness to determine the Si deposition layer thickness where the laser passes over the substrate, and also where the laser beam does not pass over the wafer. The schematic of the photoenhanced CVD (PCVD) system is shown in Fig. 1. The wafers are held on quartz pins, face down to minimize particulates, and can be heated rapidly from the back between room temperature to 900 °C by a bank of tungsten-halogen lamps. A QUESTEK ArF excimer laser output (20 ns pulses with 200 mJ/pulse at 80 Hz maximum output) is passed through a beam expander to provide a 6-cm-wide, 2-mm-high beam with a 10% uniformity along the width as determined by a Scientech power meter. The laser shines into the processing chamber, tangentially across the wafer through Suprasil quartz windows which have 80% transmittance at 193 nm. The windows are purged with 1100 sccm He to prevent deposition on them.

Prior to Si deposition, the wafers are cleaned *in situ* for 60 min at 300 °C, in 200 sccm hydrogen, at 100–300 mTorr by passing an 8 W (80 Hz at 100 mJ/pulse) laser beam tangentially across the surface of the wafer. The beam expander and laser window reduce the laser output power by a factor of 0.2. Although hydrogen does not show single-photon absorption above 110 nm, the two-photon absorption cross section at 193 nm is $[9\times10^{-33} I_o]$ cm^2, where I_o is the intensity.[9] Using second-order perturbation theory, the photon absorption increases quadratically with I_o for our process parameters leading to excited H_2 (E, F Σ_g^+) states which can subsequently lead to photoionization and photodissociation.[9] For 8 W laser output at 80 Hz, and 300 mTorr hydrogen pressure, assuming we have a nonuniform (Gaussian) profile in a vertical di-

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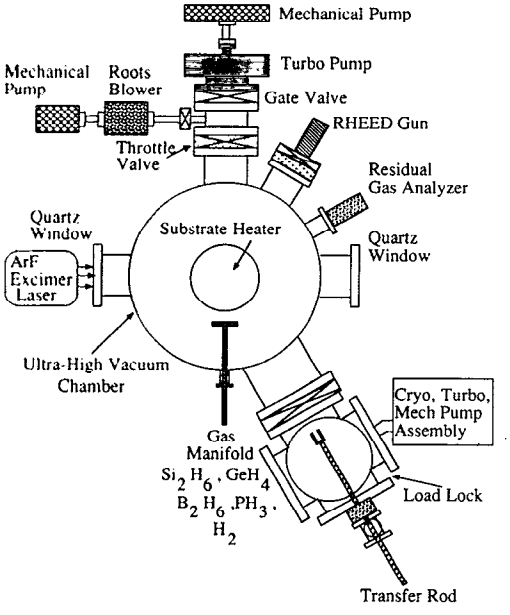

FIG. 1. Schematic diagram of PCVD system.

mension of about 0.2 mm, about 3×10^{14} hydrogen atoms could be produced by photodissociation per hour over the wafer, which can presumably further reduce the oxygen and carbon levels on the silicon surface.[7,10] The surface cleaning results in the conversion of the as-loaded (1×1) Si(100) surface into a (2×1) reconstruction pattern, as determined by *in situ* RHEED analysis along the [110] direction. A (2×1) reconstruction pattern results from a dimerization of the (100) Si surface resulting from the conversion of a Si dihydride termination produced by the dilute HF dip to a monohydride termination. The (2×1) pattern could, however, also be due to thermal desorption of hydrogen from the dihydride surface, leading to monohydride termination.[7] Nevertheless, the production of a (2×1) reconstruction pattern requires very low contamination levels, including oxygen and carbon, and hence is an excellent test for the effectiveness of the *ex situ* and *in situ* clean. Since carbon and oxygen hinder Si epitaxy, UHV processing and *in situ* surface cleaning are critical to successful low-temperature Si epitaxy. Si deposition has been achieved by flowing in 4–40 sccm of Si_2H_6 at 3–20 mTorr for substrate temperatures between 280–450 °C, and 0.5–6 W of laser power at 20–80 Hz. Controllable, uniform deposition rates (0.5–4 Å/min) have been achieved, which are low enough for superlattice-type applications. Single-crystal Si films (250 Å in 3 h at 1.4 Å/min) have been grown at 330 °C using 2 W laser power. The deposition is entirely due to photoenhancement because there is no growth where the laser beam does not pass over the wafer. At higher temperatures (450 °C), there is a thermal component of growth (1.6 Å/min) over and above photoenhanced growth (1.6 Å/min). Polycrystalline or amorphous films are deposited if the substrate temperature is lowered to 280 °C (due to insufficient adatom mobility), or if the laser power is raised to 7 W (due to high growth rates) (Table I). The growth rate increases with laser

TABLE I. Growth rates and film morphology under different deposition conditions.

Growth conditions temperature, laser power, Si_2H_6 partial pressure	Growth rate (A/min) with laser	Growth rate (A/min) without laser	Film type and morphology	% of Si precursors incorporated into film
280 °C, 0.7 W, 10 mTorr	1.3	0	amorphous smooth	15
330 °C, 2 W, 6 mTorr	1.4	0	crystalline smooth	8
330 °C, 7.6 W, 5 mTorr	3.7	0	polycrystalline smooth	7
450 °C, 1.0 W, 5 mTorr	3.2	1.6	amorphous rough	30

power, substrate temperature and Si_2H_6 partial pressure.

The crystallinity of the deposited films has been examined by *in situ* RHEED analysis where, for the epitaxial films grown at 330 °C, we see a (1×1) streaky pattern after 1 h of deposition, indicating that the films are single crystal with a smooth surface. The RHEED patterns gradually turn spotty after 4 h, indicating that the films are still single crystal, but the film morphology becomes rougher with increasing film thickness (Fig. 2). Diffuse, ring-type RHEED patterns are observed from the polycrystalline or amorphous films deposited at excessively high laser powers (7 W), or very low substrate temperatures (280 °C). The crystallinity has also been examined by selected area electron diffraction which confirms the single-crystal (100) orientation of the epitaxial layers grown at 330 °C, 0.5 W laser power (Fig. 3).

The morphology of the deposited films and evidence of stacking faults were examined by modified Schimmel etching [1:2:1.5 of CrO_3 (0.75M):HF (49%):H_2O, which has an etch rate of 70 Å/s] followed by Nomarski microscopy.

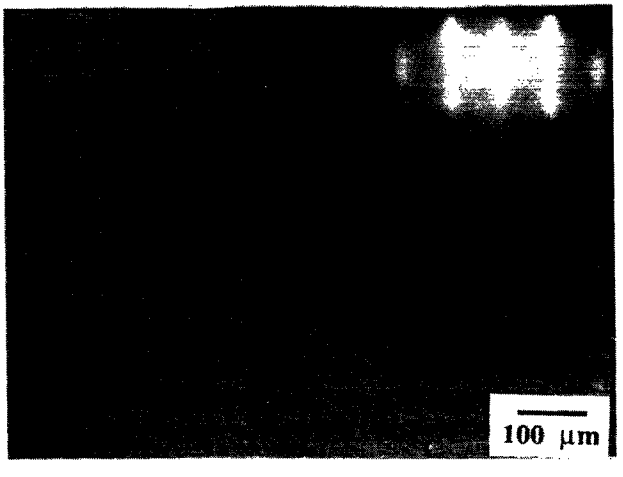

FIG. 2. RHEED pattern along [110] direction after Si photoepitaxial growth and Nomarski picture of epitaxial Si film after modified Schimmel etching.

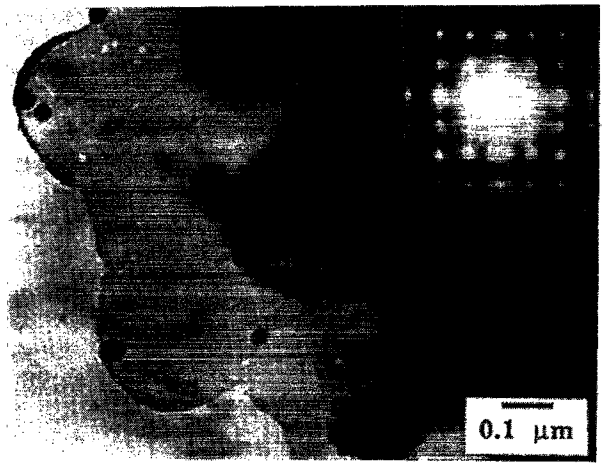

FIG. 3. Selected area electron diffraction pattern and TEM micrograph of epitaxial Si layer.

Epitaxial films grown at 330 °C, 0.5 W laser power and 10 sccm Si_2H_6 are specular, and no evidence of stacking faults are seen (Fig. 2), attesting to the low levels of oxygen and other heavy metal contamination on the starting substrate surface which could otherwise nucleate stacking faults. On the other hand, polycrystalline films with extremely rough morphology after defect etching and a ring-type electron diffraction pattern are deposited for 7 W laser power (Fig. 4). The epitaxial films grown at 330 °C and 0.5 W laser power were examined by plan-view transmission electron microscopy (TEM) (Fig. 3). Excellent film quality with no dislocation loops is observed, indicating that the dislocation loop density is below TEM detectable limits (less than 10^5–10^6 defects/cm^2).

It has been proposed that photolytic dissociation of Si_2H_6 results in the creation of SiH_3SiH and H_2 via the $2a_{1g}$–$4s$ Rydbert transition.[3] However, SiH_3SiH has not actually been detected spectroscopically. It has been suggested that SiH_3SiH absorbs a second photon creating the SiH species in the $A^2\Delta$ excited state, and SiH_3. SiH_3SiH, SiH, SiH_3, and Si_2H_6 undergo heterogeneous and homogeneous reactions leading to adsorption of SiH_2 on the hydrogenated Si surface followed by H evolution leading to Si growth. The most important pyrolytic pathway for decomposition of Si_2H_6 is the creation of SiH_4 and SiH_2. Under typical growth conditions (2 W laser power 80 Hz, 10 sccm Si_2H_6 at 6 mTorr partial pressure and 600 mTorr total pressure, 330 °C, and 1.4 Å/min growth rate), we pump in photons at a peak value of 4.8×10^{24} photons/s during the 20 ns pulse, at an average rate of 2×10^{18} photons/s. We flow in Si_2H_6 molecules at a rate of 4×10^{18} molecules/s. For this partial pressure of Si_2H_6, we have 2×10^{14} molecules/cm^3. Using this, the cross section of the laser beam and the absorption cross section of 4×10^{-18} cm^2 for Si_2H_6 at 193 nm,[2] for our chamber geometry, we estimate that 0.8% of the photons are absorbed, leading to photodissociation of Si_2H_6 into SiH_3SiH at the rate of 3×10^{15}/s under the wafer. The deposition rate, corresponding to a growth rate of 1.4 Å/min (5×10^{14} Si atoms/s deposited on the substrate), leads to an incorporation efficiency of 8%. The growth rates are observed to increase linearly with laser power, indicating that photodissociation is the rate limiting step, rather than hydrogen desorption, unlike as in other low-temperature Si epitaxial processes.[1] We have found that on average roughly 18% of the available silicon precursors generated by the laser are eventually incorporated into the film.

Si homoepitaxy on Si(100) substrates has been achieved in an UHV system at 330 °C by the photolytic decomposition of Si_2H_6 by an ArF excimer laser passing tangentially across the wafer. Growth rates of 0.5–4 Å/min are observed. The growth involves photolytic decomposition of Si_2H_6 and generation and adsorption of SiH_2 precursors on the hydrogenated Si surface, which is the rate-limiting step. Very low defect density films in terms of stacking faults and dislocation loops (less than 10^5–10^6 cm^{-2}), and excellent crystallinity have been obtained.

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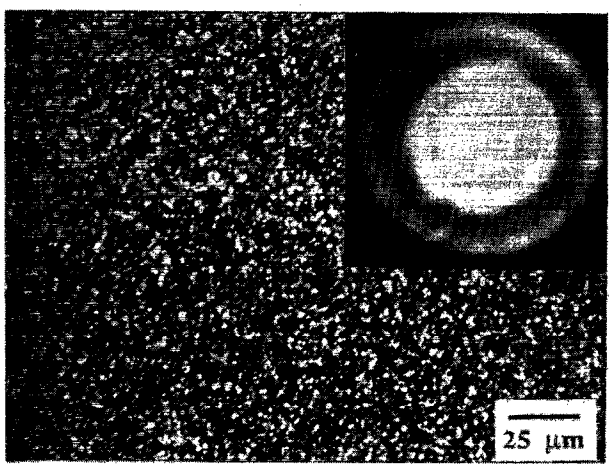

FIG. 4. Nomarski micrograph and electron diffraction pattern from polycrystalline Si film.

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