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Low-temperature RPCVD of Si, SiGe alloy, and $Si_{1-y}C_y$ films on Si substrates using trisilane (Silcore®)

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ABSTRACT

Si homo-epitaxial growth by low-temperature reduced pressure chemical vapor deposition (RPCVD) using trisilane (Si_3H_8) has been investigated. The CVD growth of Si films from trisilane and silane on Si substrates are compared at temperatures between 500 and 950 °C. It is demonstrated that trisilane efficiency increases versus silane's one as the surface temperature decreases. Si epilayers from trisilane, with low surface roughness, are achieved at 600 and 550 °C with a growth rate equal to 12.4 and 4.3 nm min^{-1}, respectively. It is also shown that $Si_{1-x}Ge_x$ layers can be deposited using trisilane chemistry.

The epitaxy of $Si_{1-y}C_y$ films as stressors source and drain is a promising way to improve the performances of n-type MOS devices. To take advantage of the tensile-strained $Si_{1-y}C_y$ films, the level of carbon into substitutional sites must be significant ($\geqslant 1\%$). Such levels of substitution require low growth temperatures (<650 °C) and high growth rates. Using trisilane and methylsilane gases, the highest substitutional carbon concentrations incorporated are 1.9% at 600 °C and 2.3% at 550 °C with growth rates equal to 20 and 7 nm min^{-1}, respectively. Stress values of about few gigapascals have been measured on blanket $Si_{1-y}C_y$ films.

1. Introduction

For future CMOS technologies (32 nm and beyond), Si epilayers, SiGe alloy layers [1,2], and $Si_{1-y}C_y$ films [3,4], are intensely studied as possible source and drain or channel materials. A non-degrading and cost-effective integration of epitaxial layers using chemical vapor deposition requires low thermal budget and high growth rate, respectively. In this context, conventional silicon precursor compounds (SiH_4, SiH_2Cl_2) are not sufficiently reactive at low temperature (<650 °C) to grow cost-effective epitaxial silicon, $Si_{1-x}Ge_x$ layers, or $Si_{1-y}C_y$ films. In contrast, trisilane (SiH_3–SiH_2–SiH_3) is a promising candidate for low-temperature CVD silicon growth because it has relatively high sticking coefficient and low activation energy for breaking the Si–Si bond. The Si–Si bond energy, E_{Si-Si} (226 KJ mol^{-1}), is lower than the H–Si bond energy, E_{H-Si} (318 KJ mol^{-1}).

In the first part of this work, the efficiency of trisilane decomposition on silicon substrates is studied. We compare the CVD growth of Si epilayers using either trisilane or conventional silane precursor. The low-temperature growth kinetics and surface roughness are addressed.

The second part deals with the growth of SiGe alloy films, using trisilane and germane precursors. The germanium incorporation as a function of the growth temperature is analysed. The crystallographic quality of $Si_{0.8}Ge_{0.2}$ epilayers grown using either trisilane or silane is compared.

In the last part, the CVD of $Si_{1-y}C_y$ films is addressed. Trisilane and methylsilane are used for low-temperature CVD $Si_{1-y}C_y$ growth. The carbon incorporation as a function of the growth temperature is analysed, and stress measurements are performed on blanket $Si_{1-y}C_y$ films using UV Raman spectroscopy.

2. Experimental details

Thin films were grown in an industrial ASM Epsilon® reduced pressure chemical vapor deposition (RPCVD) reactor, on 200 mm Si(0 0 1) substrates. In this study, the working pressure was in the range 10–760 Torr. The silicon source gases trisilane (Si_3H_8) and

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silane (SiH_4) were both used, for comparison. The trisilane material used was the epi-quality commercial Silcore® form. It is an ASM/Voltaix proprietary trisilane quality. The germanium, and carbon source gases used in this work were diluted germane (10% GeH_4 in H_2), and diluted methylsilane (5% $SiCH_6$ in H_2), respectively. The carrier gas was purified hydrogen (H_2). Its flow was kept constant at a few tens of standard liters per minute for this study.

To evaluate the kinetics of homo-epitaxial Si layers (the overall growth time is few minutes), the thickness (Γ) of the Si films was determined by differential weight (Δm) measurements (sample carried weight before and after deposition) using the following relation:

$$\Gamma(nm) = \Delta m(g) \times 1.3667 \times 10^4.$$

The thickness of homo-epitaxial Si layers is approximately 100 nm using trisilane precursor. Using silane chemistry, we should note that the thickness of the epilayers at low temperature ($<600\,^\circ C$) is about a ten of nanometers (because of the limited thermal decomposition). We should note that estimated-error from differential weight measurements is ± 5 nm. The surface roughness of the Si epilayers was analysed by atomic force microscopy (AFM). AFM was performed in a tapping mode on a Digital Instruments DI3100 NanoScope III.

The thickness of the SiGe layers and the Ge content in the SiGe alloy were analysed using a KLA Tencor SE1280 spectroscopic ellipsometer. The quality of the epilayers grown with either trisilane or silane was compared through photoluminescence (PL) analysis [5] on $Si/Si_{0.8}Ge_{0.2}/Si$ quantum wells (QW).

Regarding $Si_{1-y}C_y$ films, the layers were analysed by secondary ion mass spectroscopy (SIMS) and high-resolution X-ray diffraction (HR-XRD). The SIMS measurements were carried out on a CAMECA IMS 5F spectrometer. Cs^+ primary ions were used to evaluate the total carbon incorporation in silicon. The X-ray diffraction measurements were performed on a Philips high-resolution diffraction (X'Pert MRD) system at a Cu Kα1 wavelength of 0.15406 nm. A Philips XRD simulation program was used to fit the experimental profiles. We have adopted Vegard's law with linear extrapolations between the lattice parameters and ratios of the elastic coefficients of Si and β-SiC [6]. The good agreement between the simulated and measured (0 0 4) HR-XRD $\omega{-}2\theta$ curves enabled us to determine the substitutional carbon contents in the $Si_{1-y}C_y$ films (assuming pseudomorphic $Si_{1-y}C_y/Si$ stacks).

Stress measurements were performed on blanket $Si_{1-y}C_y$ layers using UV Raman spectroscopy [7] with a 363.8 nm laser line as excitation source.

3. Results and discussion

3.1. Low-temperature epitaxial growth of Si layers

The growth rate of silicon layers for each precursor, trisilane versus silane for a similar incoming silicon atomic flow of about 1.96×10^{21} Si atoms min^{-1}, is plotted as a function of the temperature in the 500–950 °C range (Fig. 1). The working pressure was kept constant at a few tens of Torr. Error bars are indicated for the growth rate. The Arrhenius plot of the deposition rate using silane shows well-known mechanisms [8]. Below 850 °C, the rate-limiting mechanism is surface chemical kinetics, i.e. chemisorption, surface migration, lattice incorporation, and desorption. From the slope in the 550–850 °C range, the activation energy is determined to be about 190 KJ mol^{-1} (± 20 KJ mol^{-1} with error bar at 550 °C). The activation energy is linked to the energy evaluated by Sinniah et al. [9] (196 KJ mol^{-1}). The deposition rate is limited by hydrogen desorption. At higher temperature (above 850 °C), the deposition rate is limited by mass transport.

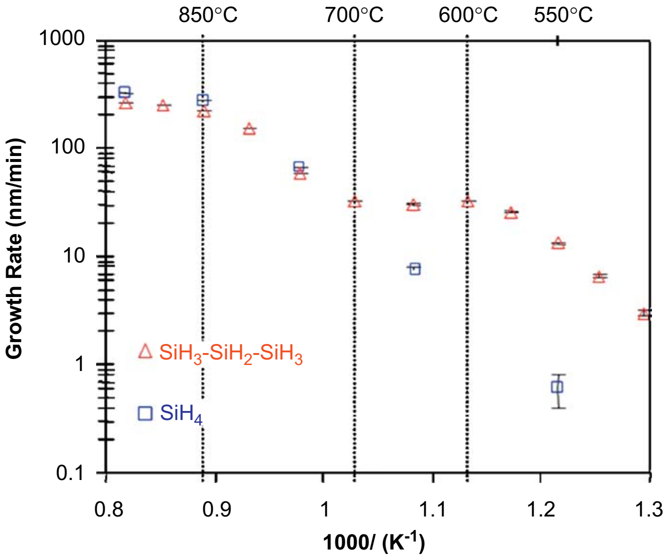

Fig. 1. The growth rate of Si layers from trisilane (Silcore®) and silane, in equivalent Si atomic flow, as a function of the growth temperature.

Regarding the deposition rate using trisilane precursor, Fig. 1 shows a more complex Arrhenius plot. Below 850 °C, the growth rate depends on the surface temperature, and it is limited by chemical kinetics. However, Fig. 1 shows an unvarying deposition rate in the 600–700 °C temperature range. The surface temperature variation does not act upon the thickness of the Si films, during a defined overall growth time. Complex pyrolysis mechanisms divide surface limited regime. From the slope in the 500–600 °C range, the activation energy is evaluated to be about 180 KJ mol^{-1}. This energy is similar to the activation energy using silane precursor. Nevertheless, the growth rate is much larger with trisilane precursor (Fig. 1). Indeed, the Si–Si bond energy, E_{Si-Si} (226 KJ mol^{-1}), is lower than the H–Si bond energy, E_{H-Si} (318 KJ mol^{-1}). Trisilane precursor has relatively high sticking coefficient on the surface from SiH_3 or SiH_2 by-products. In their article, Kulkarni et al. [10] have shown that hydrogen ad-atoms can react with strongly hydrogenated SiH_x compounds. Using trisilane chemistry, SiH_x (x=1–4) by-products can react and this leads to SiH_4 formation or decomposition via the following mechanisms:

$$H_3Si - SiH_2 - SiH_3(g) \rightarrow 2SiH_4(g) + Si(s) \tag{1}$$

$$H_3Si - SiH_2 - SiH_3(g) \rightarrow SiH_4(g) + 2H_2(g) + 2Si(s) \tag{2}$$

$$SiH_4(g) \rightarrow 2H_2(g) + Si(s) \tag{3}$$

The rate-limiting mechanism is the hydrogen desorption (free sites limited by hydrogen ad-atoms) and SiH_4 compounds can be generated. In the 600–700 °C temperature range, SiH_4 hydride formation slows down silicon growth (because of the SiH_4 limited thermal decomposition). Higher working pressures accentuate volatile SiH_4 formation. The surface SiH_4 decomposition is limited below 700 °C, and the deposition rate decreases as the working pressure increases (see Fig. 2). An unvarying deposition rate in the 600–700 °C temperature range, with a defined working pressure, is a major advantage for integration because it allows a reliable epitaxial growth of Si layers.

Above 700 °C, SiH_4 generation from reaction (1) is so immediate that the deposition rate of silicon layers for each