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Carbon re-incorporation in phosphorus-doped $Si_{1-y}C_y$ epitaxial layers during thermal annealing

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ABSTRACT

The carbon-incorporation behavior in phosphorous-doped $Si_{1-y}C_y/Si$ ($y_1 \sim 0.018$, $y_2 \sim 0.024$) epilayers grown by reduced pressure chemical vapor deposition (RPCVD) has been investigated as a function of annealing temperatures. An abnormal interstitial carbon (C_i) re-incorporation was observed in the initial stage of thermal annealing, introducing an additional tensile strain into the $Si_{1-y}C_y$ epilayers. At higher temperature but below β-SiC precipitation threshold, almost complete strain relaxation was found. These strain transitions can be attributed to the competitive behavior between C_i re-incorporation and phosphorus deactivation to kick out the substitutional carbon (C_{sub}) atoms during the post-annealing process. This work demonstrated that $Si_{1-y}C_y$ epilayers grown by RPCVD could keep both enhanced carbon incorporation and nonequilibrium phosphorus activation if the thermal budget is well controlled.

1. Introduction

$Si_{1-x-y}Ge_xC_y$ group IV alloys have attracted considerable attention due to their potential applications in Si-based optoelectronics, thermoelectrics, and band-gap engineering [1–5]. Among these alloys, researchers have proposed $Si_{1-y}C_y$ epitaxy as a potential source/drain (S/D) material to further boost the electron mobility in channel of n-channel metal-oxide-semiconductor field effect transistors (n-MOSFETs) via strain engineering [6,7]. However, carbon has a low equilibrium solid solubility in silicon ($\sim 3 \times 10^{17}$ atoms/cm^3 even at the melting point). Nonequilibrium growth techniques, such as molecular beam epitaxy (MBE) [8,9], and solid phase epitaxial re-growth (SPER) [10], are needed to incorporate more than 1% substitutional carbon into silicon lattice to generate significant strain effect. On the other hand, in order to form junction, dopants are conventionally introduced into S/D regions by ion implantation, following by high temperature annealing to activate these dopants. Due to low parasitic resistance requirement, doping level exceeding equilibrium solid solubility can be usually found in nowadays ultra-shallow junction [11]. However, the doping implantation has been reported to cause detrimental effects to highly doped $Si_{1-y}C_y$ S/D devices [12,13].

Chemical vapor deposition (CVD) is a commonly used epitaxy technique, satisfying the in situ doping needs of S/D junctions. For $Si_{1-y}C_y$ epitaxy in CVD, a high temperature is usually required for the precursors to decompose, while a low temperature regime is also necessary to freeze carbon atoms on substitutional lattice sites to avoid the formation of Si–C interstitial complexes [14]. The process window for high quality $Si_{1-y}C_y$ epitaxy is therefore defined by these two contradictory constraints. Due to its nonequilibrium nature, understanding the carbon-incorporation behavior in $Si_{1-y}C_y$ epitaxy and how dopants interact with substitutional carbon (C_{sub}) during the thermal treatment is crucial for implementation of this tuning knob in future microelectronic device. In this work, we investigated the carbon-incorporation behavior and strain relaxation of phosphorous-doped $Si_{1-y}C_y$ epilayers grown by reduced pressure CVD (RPCVD) during the post-annealing process. At the initial stage of thermal annealing, an abnormal interstitial carbon (C_i) re-incorporation into substitutional lattice sites was observed. To our knowledge, this is first observed experimentally that the tensile strain in $Si_{1-y}C_y$ epilayers could be further enhanced by the post-annealing treatment. Furthermore, almost complete strain relaxation was found at higher annealing temperature but below the β-SiC precipitation threshold. Our experimental results indicated that these strain transitions were strongly correlated with the competitive behavior between C_i re-incorporation and phosphorus deactivation during thermal annealing. We propose some mechanisms to elucidate these phenomena.

2. Experimental

10–25 Ω cm, 300 mm diameter, p-type (001)-oriented silicon wafers were used in the present study. Following a standard Radio Corporation of America cleaning process, 75-nm-thickness $Si_{1-y}C_y$ ($y_1 \sim 0.018$, $y_2 \sim 0.024$) epilayers were grown at

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550 °C in a commercial RPCVD reactor using trisilane (Si_3H_8), monomethylsilane ($SiCH_6$), phosphine (PH_3), and H_2 as the gaseous precursors. No in situ cleaning was performed before the epitaxy relying on the fact that the growth temperature is low enough to preserve hydrogen passivation on the silicon surface [15]. Subsequently, the epi-wafers were annealed by a rapid thermal annealing (RTA) process at temperatures ranging from 500 to 1000 °C for 60 s in the nitrogen ambient. After the treatments above, the strain profiles of annealed epilayers were measured by high-resolution X-ray diffraction (HRXRD) using Cu Kα_1 XRD around the (004) Si peak. The effective C_{sub} concentrations were further determined by reciprocal space mapping (RSM) around the (004) and (224) Bragg diffractions. The C_{sub} concentrations were determined to be 1.8% and 2.4% in the as-grown $Si_{1-y1}C_{y1}$ and $Si_{1-y2}C_{y2}$ epilayers, respectively. To study the configuration of local chemical bonding in the $Si_{1-y}C_y$ epilayers, Raman spectra were acquired using an Andor SR-500i spectrometer with a spectral resolution of 0.5 cm^{-1}. The Raman spectra were excited by a diode-pumped solid-state (DPSS) laser line with wavelength of 473 nm and measured at room temperature in a near-backscattering geometry. Both RSM and Raman measurements indicated that the carbon concentration was uniform across the wafer. Utilizing secondary ion mass spectrometry (SIMS), total carbon concentrations in $Si_{1-y1}C_{y1}$ and $Si_{1-y2}C_{y2}$ epilayers were confirmed to be 1.01×10^{20} cm^{-3} ($\sim$2.02%) and 1.34×10^{21} cm^{-3} ($\sim$2.68%), respectively, and the phosphorus concentrations were 3.6×10^{20} cm^{-3} and 2.4×10^{20} cm^{-3}, respectively. Transmission electron microscopy (TEM) was also performed to analyze the microstructures of annealed $Si_{1-y}C_y$/Si heterostructures. Four point probe measurements were employed to measure the sheet resistances of the stained layers and converted to the degree of phosphorus deactivation after post-annealing.

3. Results and discussion

The amount of C_{sub} can be roughly characterized from its influence on the tensile lattice distortion, which is directly related to the angular shift between the silicon substrate peak and the $Si_{1-y}C_y$ epilayer peak in the rocking curves. Fig. 1 shows the strain profile evolution for the $Si_{1-y}C_y$ epilayers as a function of post-annealing temperatures. For the as-grown samples, in addition to the Si and $Si_{1-y}C_y$ peak, interference fringes reflecting the epilayer thickness were clearly visible. For the $Si_{1-y1}C_{y1}$ ($y_1 \sim 0.018$) system shown in Fig. 1(a), a significant shift of the $Si_{1-y}C_y$ peak to the higher Bragg angles was observed at the initial stage of thermal annealing and then reached a maximum position at 700 °C, indicating an increment of C_{sub} concentration and tensile strain. This result is very interesting since to our knowledge, carbon atoms in $Si_{1-y}C_y$ epilayers usually loss their substitutional sites or even precipitate as interstitial complexes after post-annealing processes [8,16,17]. The $Si_{1-y2}C_{y2}$ ($y_2 \sim 0.024$) samples also showed the similar temperature dependence in the strain profile evolution. The only difference is that the maximum position of the $Si_{1-y2}C_{y2}$ peak was raised to 800 °C.

The effective C_{sub} concentration and strain status in the $Si_{1-y}C_y$ epilayers were further determined by HR-RSM measurements. Fig. 2 shows the HR-RSM around the (224) reflection from the as-grown and 800 °C-annealed $Si_{1-y2}C_{y2}$ epilayers, respectively. Diffracted intensity distributions were plotted as isointensity contours as a function of the reciprocal lattice vectors $k_\parallel$ parallel and $k_\perp$ perpendicular to the surface. The epilayer and substrate peaks were perfectly aligned along the $k_\parallel$ direction showing that both $Si_{1-y2}C_{y2}$ epilayers were fully strained with negligible in-plane strain relaxation within the detection limit of the instrument. Combined with the (004) HR-RSM measurements, the effective C_{sub} concentration in the $Si_{1-y2}C_{y2}$ epilayers were calculated to be 2.39% and 2.51% for the as-grown and 800 °C-annealed samples, respectively. It indicated that there was indeed an additional carbon source incorporated into the substitutional lattice sites during the post-annealing treatment. With further increasing annealing temperatures to 900 °C for both $Si_{1-y}C_y$ systems, as shown in Fig. 1(a) and (b), more significant shifts of the $Si_{1-y}C_y$ peaks back to the substrate were observed, implying plenty of C_{sub} loss or deactivation. The above experimental observations give rise to some fundamental questions. First of all, what is the strain enhancement mechanism at the initial stage of thermal annealing? Second, compared to previous $Si_{1-y}C_y$ post-annealing studies [18,19], our experimental observation shows much enhanced relaxation in the lower-temperature regime. Usually very high temperature or very long time treatment is needed to result in such high degree of strain relaxation. What then are the strain relaxation pathways for these $Si_{1-y}C_y$ samples in our system? Furthermore, the $Si_{1-y2}C_{y2}$ sample seemed to exhibit a better thermal

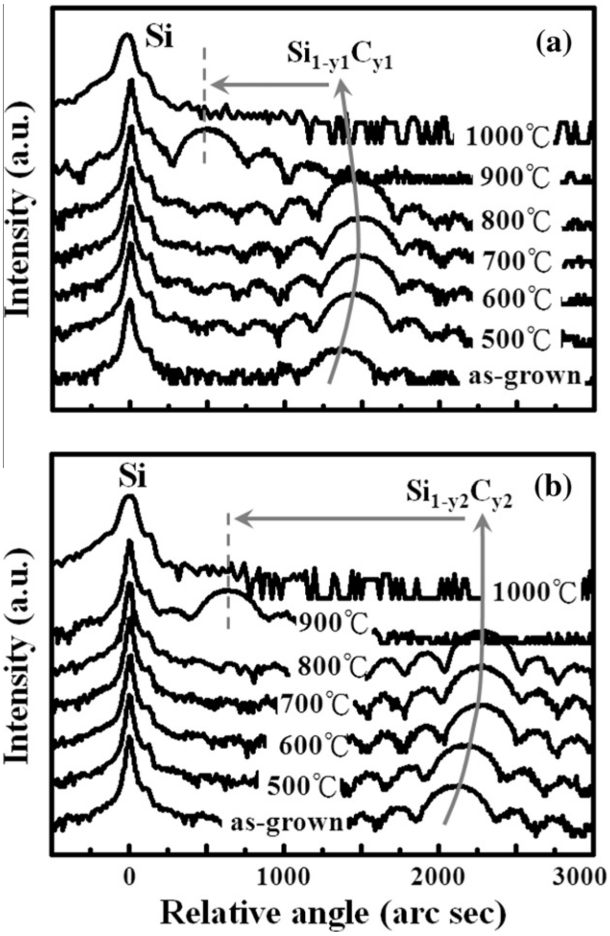

Fig. 1. HRXRD (004) rocking curves for (a) $Si_{1-y1}C_{y1}$ and (b) $Si_{1-y2}C_{y2}$ epilayers post-annealed at various temperatures, respectively.

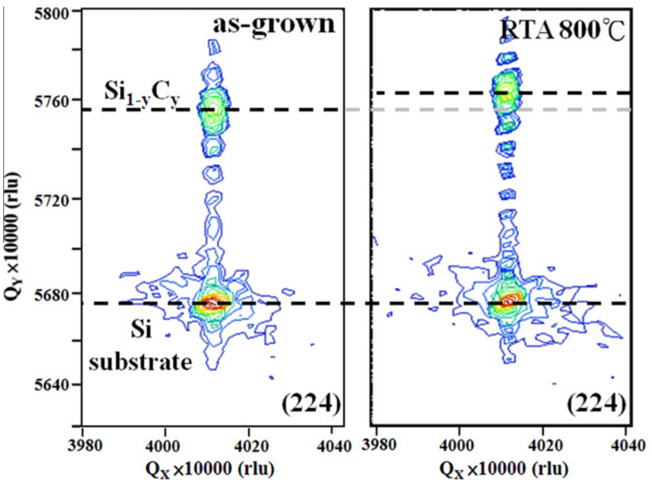

Fig. 2. Asymmetric (224) HR-RSM of as-grown and 800 °C-annealed $Si_{1-y2}C_{y2}$ samples, respectively.