Epitaxy of carbon-rich silicon with MBE

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Abstract

At high concentrations, carbon in silicon shows some properties of technological interests like gap engineering, lattice engineering or the reduction of the so-called ‘Transient Enhanced Diffusion’ of some dopants. The carbon incorporation in concentrations above 1% is nevertheless a difficult task due to the low carbon solubility in silicon. Here, we present a systematic approach of the $\text{Si}_{1-x}\text{C}_x$ layer growth by Molecular Beam Epitaxy (MBE). To study the influence of the growth temperature on the carbon incorporation, we deposit 100 nm thick silicon layers with different carbon concentrations separated by a 100 nm silicon spacer for different temperatures, ranging from 370 up to 800 °C. In-situ Reflection High Energy Diffraction (RHEED), Secondary Ion Mass Spectroscopy (SIMS) and cross-sectional Transmission Electron Microscopy (TEM) have been performed to characterize the as-grown structures. We show the presence of two distinct growth phenomena, a ‘classical’ one, around 450 °C, where carbon is mainly substitutionally incorporated, defect free until 2%; and a second one, above 550 °C, showing an agglomeration of carbon in thin layers with presumably a very high local concentration, without any planar defects. We propose in this work a diagram of Si:C growth by MBE. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon (C) has been considered for a long time as an impurity to suppress in silicon (Si). Only recently, it regained interest since it has been found [1] that the carbon incorporation can reduce or even suppress the so-called ‘Transient Enhanced Diffusion’ of dopants like boron or phosphorous. The suppression of this uncontrolled diffusion of dopants during, for example thermal budget, has been described [2] as a relationship between the C oversaturation and the Si point defects created. This effect opened up the possibility to fabricate Si–Ge based heterobipolar transistors with a very narrow base region (due to the suppressed diffusion of the boron base doping) important for ultra-high frequency applications [3–5]. A carbon concentration between 0.1 and 1.0% is usually used. Besides, the carbon incorporation in the substitutional lattice creates tensile stresses which can compensate the stresses due to germanium incorporation in Si, reducing the misfit between Si and SiGe layers. A SiGeC alloy with 10% Ge and 1% C has the same lattice parameter than Si [4].

The C solubility in Si is as low as few ppm at melting temperature. Different kinds of growth methods have been tried for the incorporation of high C concentrations. Implantation [6] requires usually high temperatures to repair the implantation damages leading often to the SiC precipitation. Therefore, kinetically controlled methods are preferred. The Chemical-Vapor-Deposition (CVD) has been tried with some success [7,8]. We focus here on Molecular Beam Epitaxy (MBE) used for the first time by Iyer et al. [9] to growth $\text{Si}_{1-x}\text{C}_x$. Since that time, many attempts have been done achieving concentrations as high as 5% without defects but for layers not thicker than 10 nm [10] leading to pseudomorphic growth. A draft-phase diagram has been proposed by Powell et al. [11] but it does not take into account the self-organized structures observed by Simons et al. [12] and supposes a SiC precipitation not experimentally seen so far.

To get a general view of the $\text{Si}_{1-x}\text{C}_x$ growth by MBE, we choose to deposit 100 nm thick layers with different C concentrations, over a wide temperature range and characterized them by Reflection High Energy Diffraction (RHEED), Secondary Ion Mass Spectroscopy (SIMS) and cross-sectional Transmission Electron Microscopy (TEM).

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2. Experiments

We used a commercially available RIBER Siva 45 MBE with an optimized LN2 cryostat. The Si and C sources were electron-beam evaporators, which stability, better than 10%, was controlled by quadrupole mass spectrometers. The measured ratio of C dimers to C monomers present in the beam amounted about 25%. The C source is a high purity pyrolytic graphite target. The base pressure and the working pressure are in the 5×10^{-11} and 2×10^{-9} mbar range, respectively. RHEED was performed in-situ with an energy of 30 kV. The temperature of the wafers was initially calibrated with thermocouples cemented on a wafer, and later monitored during the growth by a pyrometer working in the 10–30 μm range. Thereby, we have a precision better than 10 above 400 °C.

We used 5 in. diameter (001) CZ-substrates n or p (1–10 $\Omega\text{ cm}$) doped. A standard RCA I and RCA II cleaning procedure was performed before inserting the wafers in the growth chamber. They were heated at 850 °C for 30 min to remove the protective SiO_2 layer. Afterwards, a perfect 2×1 reconstructed Si (001) flat surface could be observed by RHEED. We chose a Si growth rate $0.5 \text{ \AA s}^{-1}$. At first, a 75 nm thick Si-buffer layer was deposited, followed by a multilayer structure of 100 nm thick $\text{Si}_{1-x}\text{C}_x$ /100 nm thick Si. The layers were grown at a constant temperature with an exception for the lowest temperature, i.e. 370 °C where Si spacers were deposited at 450 °C for a better crystallinity. At the end of the each layer deposition, the shutters are closed for 1 min to take a RHEED picture without the noise of the electron gun sources. Depending on the quality of the RHEED signal, the growth is stopped to start, at the same temperature, on a new substrate, stress and free of twinning. Our samples contain 4–6 Si:C layers of different C concentrations. A Si-cap layer of 10 nm was deposited at the end of each experiment. For TEM examination, samples were prepared using standard ion milling procedures. Cross-

sectional TEM has been performed in a microscope Philipps CM20 with 200 kV and, for high resolution, in JEOL JEM 4010 microscope with a 400 kv voltage, respectively.

3. Results

During growth, RHEED is an information-rich tool to characterize the structure of the as-grown surface. We classified the RHEED pattern obtained in six groups, as presented in Fig. 1. The vertical strikes of Fig. 1A and B correspond to a perfect 2×1 reconstructed Si (001) flat surface. The slight broadening of the lines in Fig. 1B are caused by the stresses induced in the lattice by the C incorporation. In the case when the structure is getting highly stressed, i.e. when the C concentration is too high and/or the temperature do not allow the relaxation of the layer, a 3-dimensional (3-D) growth is observed with dots close to the main reflection in the [11] directions (cf. Fig. 1C, D and E). With even more stresses introduced in the lattice, twinning appears along $\{111\}$ as in Fig. 1D and E. The RHEED picture in Fig. 1F proves a polycrystallinity. Results from RHEED pictures collected for different growth temperature and C concentrations measured by SIMS, allow to draw a draft diagram of C incorporation as represented in Fig. 2. First, a growth optimum seems to exist around 450 °C. At this temperature, a 100 nm thick layer with a C concentration of 1.8% has been deposited without noticeable twinning (cf. Fig. 3B) and until 5.0%, the grown layers were crystalline. Above and below 450 °C, 3-D growth then twinning appeared for even lower carbon concentration. Below 400 °C, a C concentration above 3.0% leads to amorphous layers.

Second, above 550 °C, we noticed a retardation of the defects: whereas 3-D growth appears relatively early, i.e. around 1% carbon, the crystal starts to be twinned for higher C concentration with increasing

Fig. 1. RHEED pictures of a Si (001) surface showing (A) a clean surface, (B) a stressed lattice, (C) a 3-D growth, (D) and (E) twinning and (F) polycrystallinity. The micrographs are taken from samples grown at 450 °C.

Fig. 2. Phase diagram of the C incorporation into silicon versus the growth temperature. The studies have been done for 100 nm thick Si:C layers epitaxially grown by MBE on a Si substrate (growth rate 0.5 Å s^{-1}).

growth temperatures: 3% C at 600 °C, 4% C at 650 °C and 6% C at 700 °C. Polycrystallinity was not even achieved at 15% C at 700 °C. This behavior can not be alone explained by a more pronounced 3-D growth, and another incorporation mechanism of carbon, for such high temperatures is expected and can be seen by cross-sectional TEM.

Cross-sectional TEM investigations have been applied to cross-check the surface information given by RHEED. Fig. 3 shows examples of the structures obtained at 370, 450 and 660 °C. At the lowest temperature, an alloy with 1.7% carbon could be grown without any noticeable defects (this highest defect free concentration is higher than at 400 °C due to the temperature profile used, i.e. buffers layers deposited at 450 °C, helping the reconstruction of the structure) whereas at

2.6% a highly twinned structure was observed. A carbon concentration of 3.4% induces, at this temperature and at the early stage of the deposition, an amorphous layer. At 450 °C, until 1.8% the Si:C layers shows a strain contrast but no extended defects. Twinning then appears and propagates in the Si interlayer to the sample surface.

Above 550 °C, striations perpendicular to the growth direction in the Si:C layers were observed (Fig. 3C). With an increasing growth temperature, they become even more remarkable as a chaplet of O-dimensional (OD) defects, allowing a reduction of the stresses in the grown layers. Such self-organization of the carbon has been already detected in samples grown at 600 °C by gas phase MBE [12] and at 725 °C by CVD [7]. In Fig. 3C, one can notice the absence of contrast in the layer grown at 660 °C showing that some relaxation occurred. No twinning was detectable. The striations seem to be regularly spaced, by about 9 nm, independently of the C e-gun flux, until twinning perturbs the structure. High-resolution TEM of such planar segregations (cf. Fig. 4) suggests a pseudo amorphous segregation, 1 nm thin. Finally, it should be noted that no SiC precipitates have been seen in such layers grown below 700 °C. Above 700 °C and at high carbon concentrations, some precipitates located at the intersection of twins show typical Moiré fringes.

4. Discussion

Carbon is incorporated mainly substitutionally in silicon. Since C atoms are much smaller than the Si atoms, the C solubility is extremely low. On the other hand, the surface solubility as defined by Tersoff [13], i.e. the solubility in the first mono-layers is orders of

Fig. 3. TEM cross-sections of MBE samples grown at 370, 450 and 660 °C. The C concentrations represented here are measured by SIMS.

Fig. 4. High resolution TEM pictures of a Si:C layer deposited at 660 °C with a global C concentration of about 1.7% C. The periodic striations have often a shape as a chaplet, magnified demonstrated in the right. Notice the faceted growth surface (left).

magnitude higher due to free bonds and the perturbation of the bulk symmetry. This mechanism is strongly dependent (i) on the surface diffusion, i.e. the temperature, and (ii) on the density of ad-atoms, i.e. the growth rate. Therefore, a C concentration far above its bulk solubility can be achieved up to few percents. At low temperature (< 550 °C), no relaxation can occur besides by twinning of the grown layer. A temperature of 450 °C seems to be the optimal temperature for a perfect Si:C layer deposition at our experimental conditions. We achieved, e.g. 1.8% C into a 100 nm layer without defects. Other authors have also noticed an extremum around this temperature range, e.g. at 550 [4,11] or at 400 °C [14]. These differences might be caused by the different growth rates or due to the difficulty to measure accurately the wafer temperature in a MBE chamber.

With increasing temperature, the amount of C substitutionally incorporated relatively decreases as measured by X-ray diffraction [15], showing the presence of an interstitial position of C. Above 550 °C and in particular beyond 630 °C an other Si:C phase than the metastable substitutional carbon in Si seems to appear, which might be the reason for the parallel striations in Fig. 4. Above 650 °C, the lines are formed by chaplets of precipitates visible as a high strain contrast. Some aggregates seem to be amorphous but no SiC precipitates could be detected. According to the local strain near those aggregates, we suppose that they correlate to a C-rich phase. Rücker et al. [16] presented some ab-initio calculations showing the possibility of a Si_nC phase with $n > 4$ as a stable phase. A local C concentration of about 20% is then presumed. XPS measurements [4] performed in-situ during annealing shows a shift of the carbon 1s peak from 283.5 to 282.8 eV between 500 and 800 °C, convincing of a different Si:C phase. The SiC binding energy lies by 282.6 eV.

The 100 nm Si spacers are thick enough to reconstruct a perfect Si lattice. Nevertheless, highly 3-D or highly twinned structures can not be reconstructed in a flat defect free surface with only a 100 nm silicon

interlayer. It seems although that the repetition of the growth for the same temperature but starting with higher C concentrations shows not notable differences. We then suppose the growth of the Si:C layers being independent from the precedent ones. This seems not to be the case for temperatures higher than 650 °C where the relaxation seems to be gradually achieved in the Si:C layers. The Si:C lattice obtained after a few C rich layers at such high temperatures should have a reduced constant in the [110] directions, reason for the 3-D growth when depositing Si on such layers. The hills formed are about 10 nm high, i.e. the thickness of the deposited cap layer.

In addition, we would like to focus attention on the difficulty to measured accurately with SIMS such high C concentrations. In the percent range, relation between the amount of ionized atoms (measured) and the total dopant concentration may not be linear anymore, leading to even higher concentrations than supposed here.

5. Conclusion

We have studied the incorporation of carbon into silicon layers by MBE. The goal was directed to investigate the influence of growth parameters (temperature, carbon flux) on receiving a high carbon concentration in the range of up to several percent. A 'phase diagram' of C concentration versus growth temperature shows a complex behavior, including regions of pseudomorphic structure, defects and precipitation. In dependence on the substrate temperature, we found two regions showing distinct growth behavior: (i) in a region at around 450 °C we found a nearly complete substitutional incorporation of carbon in the Si lattice, (ii) At higher temperatures, especially > 630 °C, an inhomogeneous segregation of a Si_nC phase could be observed. This segregation is related to periodic striations/chaplets perpendicular to the growth direction.

In general, we achieved 100 nm thick layer with a C concentration up to 2.0% C without any defects. It was also possible to incorporate a higher content (above 10%) especially at higher temperatures, however, then the alloy is getting more inhomogeneous. Concerning the lattice strain of such a mismatched Si/Si:C heterostructure, a relaxation of the Si:C layer was observed. Such a growth surface with a reduced lattice constant can be applied for the epitaxy of other crystal films.

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