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In situ preparation of Si p-n junctions and subsequent surface preparation for III-V heteroepitaxy in MOCVD ambient

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ABSTRACT

III-V integration on active Si-bottom cells promises not only high-efficiency multi-junction solar cells but also lower production costs. *In situ* preparation of an adequate Si p-n junction in metalorganic chemical vapor deposition ambient is challenging, particularly since the final Si surface should be atomically well-ordered to enable low-defect III-V nucleation. Precisely, a single-domain Si(100) surface with double layer steps needs to be prepared in order to suppress antiphase disorder in subsequently grown III-V layer structures on top of the Si p-n junction. We first investigate the formation of a n^+-type collector in Si(100) as a result of annealing in tertiarybutylphosphine (TBP) or tertiarybutylarsine (TBAs) ambient. We illustrate how the n-type doping concentrations and their depth profiles depend on the essential preparation parameters, such as precursor partial pressures, exposure and annealing time, as well as reactor pressure. Subsequently, by applying *in situ* reflectance anisotropy spectroscopy, we find that exposure of Si(100) to TBP or TBAs leads to atomic disorder on the surface. Further, we apply an additional annealing step without precursor supply leading to predominantly (1×2) reconstructed Si(100) surfaces, which are suitable for subsequent low-defect III-V growth.

1. Introduction

Multi-junction solar cells based on III-V compound semiconductors today reach photovoltaic conversion efficiencies beyond 45% [1]. Replacement of the currently applied expensive substrates such as Ge, InP or GaAs by large Si wafers promises a reduction of the production costs. Moreover, Si exhibits a bandgap close to optimum for application as bottom cell in dual-junction tandem devices [2,3] and is also of interest for direct solar water splitting [4,5]. Typically, III-V solar cells are grown by metalorganic chemical vapor deposition (MOCVD), which enables upscaling of device throughput at industrially relevant scale. However, for a single growth run of the entire device structure, also the Si p-n junction has to be prepared in the MOCVD reactor, which has proven to be challenging [6,7]. In photovoltaic application, the p-n junction serves as a charge separating contact to separate holes and electrons efficiently after generation. The cell design discussed here is based on a p-type absorber, which corresponds to the lower doped substrate, and a highly doped n^+-type layer on top, which serves as a semipermeable membrane for electrons, *i.e.* an electron collector [8] (which often is also referred to as emitter). Collectors in appropriate Si bottom cells with thickness less than 0.25 µm and high doping level concentrations ($>5\cdot10^{18}\ \mathrm{cm}^{-3}$) should ensure efficient charge separation with high short circuit current densities and open circuit voltages [9].

Growth processes in MOCVD environment are highly complex, not only due to the large parameter space and chemical reactions involving the precursors. Also residues in the reactor from previous processes, as well as the process gas itself may interact with the growth surface, where, in addition, kinetic and thermodynamic driving forces compete with each other. Si(100) surface preparation in H_2-based MOCVD ambient has recently been studied by our group in great detail: Si surfaces in rather clean processing conditions were found to be H-terminated [10–12] and control over surface kinetics is indispensable to prepare Si surfaces suitable for III-V nucleation [13–15]. III-V species in the reactor can highly affect the formation of the III-V/Si heterointerface [16–18] and As-modification of Si surfaces allows to control the sublattice orientation of the III-V epilayers [19,20]. In this context, reflection anisotropy spectroscopy (RAS) [21–23] has been established as a surface sensitive *in situ* probe to identify the Si surface reconstructions during processing.

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Regarding the preparation of the Si p-n junction, it can be advantageous to apply elements for doping, which are already involved in the III-V processing such as arsenic (As) and phosphorus (P). Besides the control of the III-V sublattice orientation [19,20], As facilitates Si deoxidation [24,25], prevents out-diffusion of Si in the GaP epilayers[26]and enables the growth of GaAsP graded buffers [27] or GaPNAs solar cells [28]. Moreover, As is mostly present in realistic MOCVD growth scenarios. Phosphorus, on the other hand, was found to bind to Si during GaP nucleation [16] and is inevitable for pseudomorphic GaP nucleation [29,30] as well as lattice-matched GaPN growth.

Phosphorus in-diffusion into Si by annealing under phosphine supply in CVD ambient has already been shown to be suitable to form a p-n junction [31]. However, the exposure of Si to PH_3 leads to a roughened, two-domain Si(100) surface, which would induce antiphase disorder in subsequently grown III-V layers [7].

Here, we will study the in-diffusion into Si(100) during annealing under supply of the corresponding precursors [32] tertiarybutylphosphine (TBP) and tertiarybutylarsine (TBAs). Doping profiles will be analyzed in dependence on the annealing conditions. We will analyze the morphology of the surfaces after dopant in-diffusion and apply *in situ* RAS in order to prepare single domain, double layer stepped Si(100) surfaces for subsequent III-V nucleation.

2. Experimental

All samples were grown in a horizontal AIX-200 MOVPE reactor (Aixtron) with H_2 as process gas. We used p-type Si(100) substrates with 2 ° miscut towards [011] direction. After thermal deoxidation (1000 °C, 30 min, 950 mbar) [33], a nominally intrinsic homoepitaxial Si buffer was grown (about 200 nm) and the preferentially (1×2) reconstructed, monohydride-terminated Si(100) surface was prepared [13]. The samples were then annealed in TBP or TBAs, at 650 °C and 670 °C respectively, for group-V in-diffusion. For two series of experiments we did use different quartz parts, susceptor and carrier: The reactor parts, in which we annealed the Si samples under TBP, have never been exposed to the TBAs precursor. Prior to each Si process, the reactor was annealed at 1010 °C in 950 mbar, in the H_2 for 30 min to decrease the amount of GaP residuals present from previous runs [18]. After the in-diffusion step, on selected samples, we applied additional annealing without the precursor supply: the TBP source was closed and the samples were slowly heated up to 830 °C (heating rate of ~ 22 °C/min), where the surface was annealed for one minute before being cooled to 730 °C. This temperature is the established temperature to prepare A-type double layers steps on Si(100) surfaces with 2° miscut in a "clean" MOCVD ambient [13]. The entire process was controlled *in situ* by RAS [23] on the Si(100) surface. The spectrometer (LayTec EpiRAS-200) was aligned such that the difference in complex reflection along [011] and [0$\bar{1}$1] was measured:

$$\frac{\Delta r}{r} = 2\frac{r_{[0\bar{1}1]} - r_{[011]}}{r_{[0\bar{1}1]} + r_{[011]}}. \tag{1}$$

The intensities of the RA spectra are normalized to the Si(110) standard [21].

Selected samples were transferred by a contamination-free UHV transfer system [34] to low energy electron diffraction (LEED, Specs ErLEED 100-A) to investigate the surface reconstruction. Carrier concentration profiles in the Si samples were obtained *ex situ* by electrochemical capacitance voltage profiling (ECV, WEP-CVP21) with 0.1 m NH_4HF_2 solution (applying forward bias for p-type layers and UV illumination for n-type layers). AFM was measured in tapping mode (Bruker Dimension V) and evaluated with WSxM [35]. Selected samples were measured by energy-dispersive x-ray spectroscopy (Hitachi S-4800 II system with an EDX – NORAN System 7 from ThermoFisher Scientific).

3. Results and discussion

3.1. In-diffusion into Si(100)

We investigated the in-diffusion in dependence on duration, precursor source and reactor pressure measuring free carrier concentration profiles by ECV. It was shown in the literature that the free carrier concentration level profiles obtained by ECV are often comparable with the level of doping concentration obtained by secondary ion mass spectrometry (SIMS) measurements [6,36]. The ECV only measures electrically active carriers and is not chemically sensitive. Fig. 1 shows ECV profiles after annealing Si(100) substrates in TBP in dependence on process parameters. In general, we observe that annealing in TBP ambient creates a collector in the previously, nominally intrinsic Si buffer layer with doping concentrations as high as 10^{18}–10^{19} cm^{-3}. The doping levels of all samples exhibit a flat plateau. The n-type region thickness at a doping concentration of $1{\cdot}10^{18}$ is in the range of 100–260 nm in dependence on annealing time and reactor pressure. Longer annealing and lower reactor pressure increase the thickness of the collector. Reduction of the exposure time of the sample to TBP from 20 min (orange lines) to 10 min (blue lines) at a reactor pressure of 950 mbar (maintaining the same TBP-partial pressure, p_{TBP}) leads to reduced free carrier concentration levels, from $9{\cdot}10^{18}$ cm^{-3} to $1.5{\cdot}10^{18}$ cm^{-3}. In addition, the longer annealing time of 20 min (orange line), leads to a larger collector thickness of more than 250 nm as compared to that after 10 min annealing (blue line) of 150 nm. The annealing in TBP at 950 mbar for 10 min at higher p_{TBP} (green line as compared to blue line) results in a higher free carrier

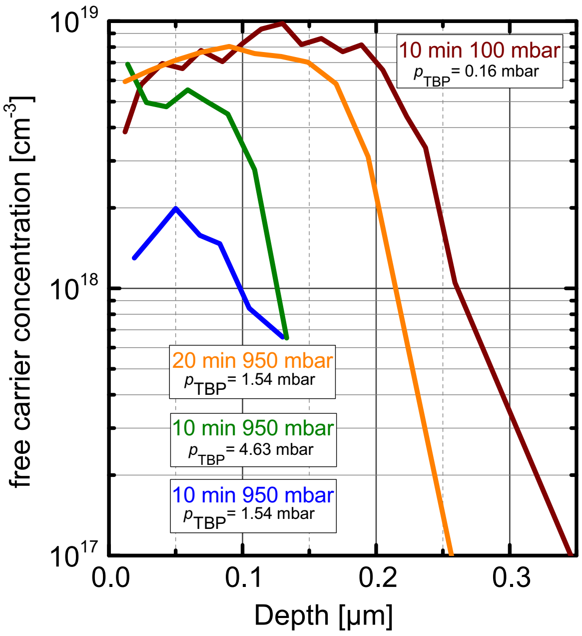

Fig. 1. Carrier concentrations in Si(100) n-type region after annealing in TBP applying different process preparation.