Heteroepitaxial Layer Overgrowth of GaP on Structured Silicon Surfaces

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Recently we have shown that the nucleation of GaP on silicon is highly selective with regard to patterned SiO_2 coated surface region. In this paper we present further studies on the heteroepitaxial overgrowth of structured Si(001) substrates by GaP. This includes epitaxial layer overgrowth of SiO_2-masked silicon wafer. The defect structure in the heteroepitaxial films is investigated by transmission electron microscopy and is related to the results of real-time monitoring of the nucleation and overgrowth kinetics by p-polarized reflectance (PR) and laser light scattering (LLS) under the condition of pulsed chemical beam epitaxy. The interpretation of the results of optical monitoring is supported by atomic probe imaging of the silicon surface in early stages of nucleation and heteroepitaxial overgrowth.

INTRODUCTION

The understanding and control of defect formation as well as the interactions and propagation of defects during later stages of compound heteroepitaxy growth represent a key target of contemporary materials science and engineering in particular, III-V compound/silicon heterostructures are of interest for a variety of applications, but are not available at present with sufficient quality due to defect formation during the initial phase of nucleation and coalescence of the heteroepitaxial film. Recently, we reported on the growth selectivity of GaP on masked Si(001) in the context of defect formation. Highly selective growth, that is, a substantially larger kinetic barrier to nucleation of GaP or $Ga_xIn_{1-x}P$ on the SiO_2-masked surface areas as compared to the bare silicon window areas has been reported [1,2] for chemical beam epitaxy at low substrate temperature of around 350°C. This is a detriment since forced overgrowth of surface area contaminated by either oxygen, carbon, or fluorine may result in the generation of strain, causing the formation of dislocations, or, for amorphous contaminants patches inducing loss of registry to the underlying substrate lattice, may result in the formation of stacking faults [1]. As a result, surface preparation and conditioning prior to growth is of utmost importance in epilayer growth processes. On the other hand the overgrowth of SiO_2 masked Si (001) may provide a means for the control of defect propagation, which is the topic of this paper.

Low temperature growth processes have been extensively investigated in the past two decades to address the problem associated with high diffusivity of impurities, thermal and lattice mismatch. As the growth temperature is reduced, the problem associated with thermal mismatch is reduced and may in many cases be excluded from consideration in the context of the origin of defects. For example, the growth of epitaxial GaP on silicon has been achieved at temperatures below 350°C [2-4] with chemical beam epitaxy and around 700°C with metal organic chemical-vapor deposition [5]. At this temperature range thermal effects are negligible in the case of GaP to be considered as a source of planar defects that are observed in the GaP epilayers. The lattice mismatch issue is currently being dealt with in a scheme that reduces coherency stress, that is, for example in the growth of compositionally graded relaxed buffer layers[2,6]. Several other techniques for control and understand-

ing of defects behaviors may be applied, such as, the epitaxial growth on patterned areas [7-9], and thermally step-graded layers [10] or thermal cyclic processes.

In this paper we use the growth of GaP/Si (001) heterostructures by pulsed chemical beam epitaxy as an example to present various options for controlling the propagation of planar defects on patterned surfaces. We present results on the real-time monitoring [11]of low temperature epitaxial growth during initial nucleation stage of GaP on silicon in correlation with the atomic force microscopy analysis.

EXPERIMENT

In this paper, we use pulse chemical beam epitaxy[2] to achieve low temperature growth of the epi-GaP films on silicon. The silicon substrate is RCA cleaned , followed by a short HF deep prior to loading in the reactor through a load lock chamber. P-polarized reflectance (PR), described elsewhere [10], and Laser light scattering (LLS) are used to monitor heteroepitaxial film growth under pulsed chemical beam epitaxy conditions, that is, the surface of the substrate is exposed to pulsed ballistic beams of tertiarybutyl phosphine [TBP, $(C_4H_9)PH_2$] and triethylgallium [TEG, $Ga(C_2H_5)_3$ at typically 300-450°C to initiate nucleation and overgrowth of the silicon substrate by an epitaxial film. The schematic representation of the experimental arrangement for the system has been presented elsewhere [1]. The switching of the sources is synchronized with the data acquisition of the PR and LLS signals to correlate the changes in the reflected intensity to the changes in the optical properties of the heteroepitaxial stack that encompass chemistry-induced changes in the surface composition and changes due to the thickness and optical properties of the growing epitaxial film. A growth cycle time of 3 seconds is used for the growth of GaP layer.

RESULTS AND DISCUSSION

Information on the very early stage of nucleation, in particular, which is directly related to growth kinetics and thickness of the growing film is revealed by the time evolution response of PR intensity to variations in the source vapor cycle and perturbations of the steady-state surface composition [3,12]. Figure 1 is the spectrum of the temporal evolution at two different angles (70° and 75°) showing the response in the p-polarized reflectance (PR) signal to exposure of the Si(001) substrate surface to alternating pulses of t-butylphosphine and triethylgallium at 350°C substrate temperature. This spectrum includes the heat up period from 0 to 300 seconds, the growth period from 300 to 330 seconds, and cool down period starting at 330 seconds. the change in the reflected intensity during the heat up and cool down periods is primarily related to the temperature dependence of the dielectric function of the substrate and surface film. More information on the characteristic features of p-polarized reflectance spectroscopy can be found in ref. [13].

The nucleation of the GaP film occurs after a brief incubation period as shown in the insert of Fig. 1. which is showing the entire growth cycle of 30 seconds from 300 to 330 seconds. Pulsing is first initiated at 300 sec and repeat every 3 sec. After an incubation period of 2-3 cycles a response is observed that shows changes in the chemistry on the silicon surface. Note that such changes can be related to built-up of a surface reaction layer [13] and changes in surface reconstruction, so that they do not necessarily imply nucleation of a film of GaP, requiring the utilization of independent methods to verify the latter. Figure 2 shows the change in surface roughness with increasing exposure time to TBP and TEG. It is observed that sample roughness increases dramatically above 20 sec of exposure to precursors. Below 20 seconds, the change in surface roughness is minimal, which is indicative of the incubation period. This is reflected in Fig. 1 insert as small fine structure with small amplitude when growth is first initialed. At the end of the period investigated here, nucleation and partial coalescence of nuclei into larger islands has occurred, as revealed by atomic force microscopy (AFM) image in Figure 3.

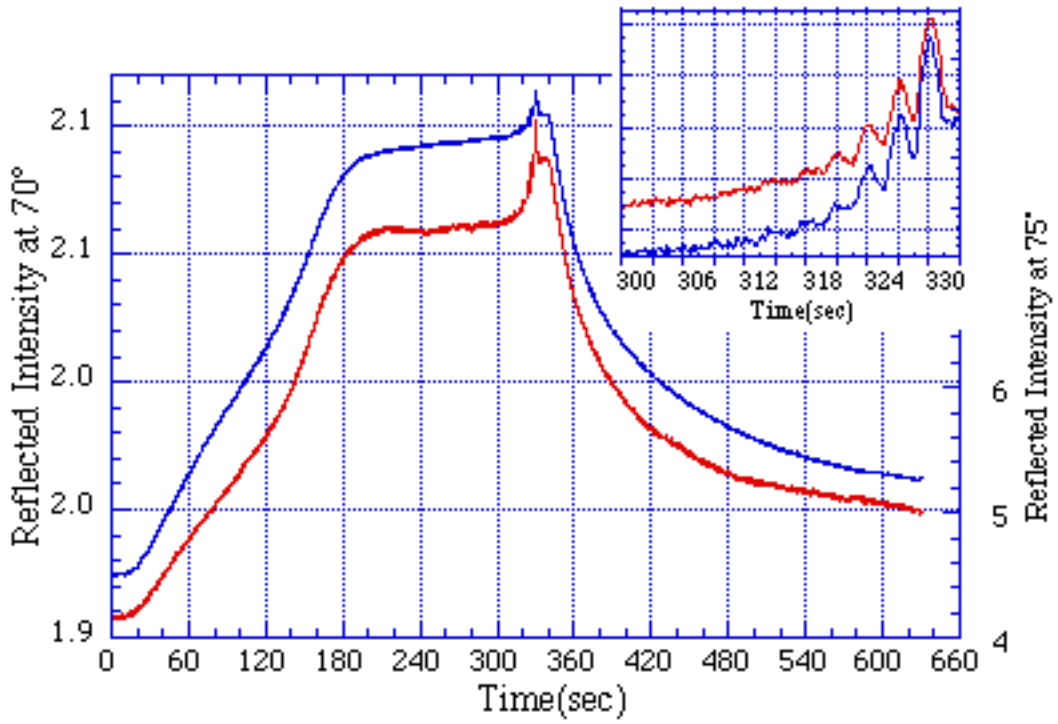


Figure 1: Time evolution of the reflected intensity at 70 and 75° after 30 seconds growth (10 cycles). The insert plot is the enlargement of the entire 10 cycle growth time after a precondition time of 300 seconds.

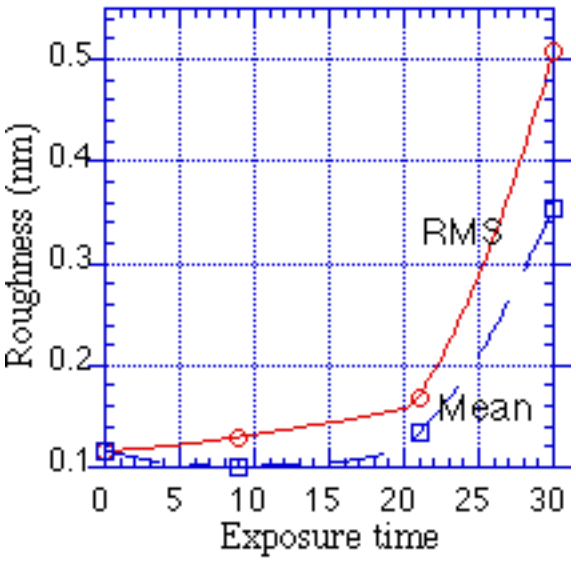


Figure 2: Shows RMS and mean surface roughness change with increase exposure to TBP and TEG.

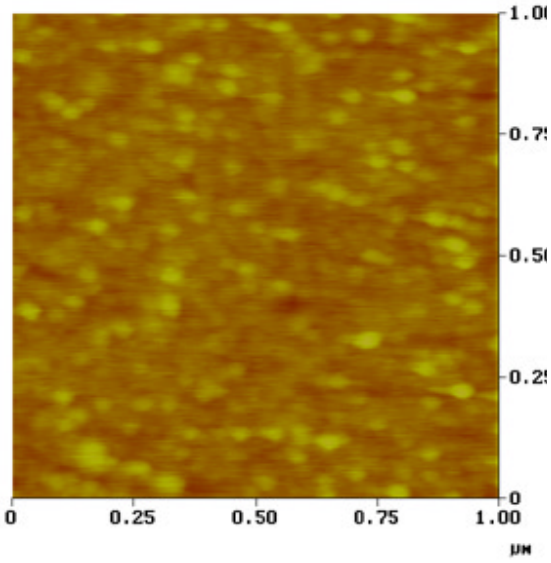


Figure 3: Atomic force microscope image of the surface after 30 seconds exposure to TBP and TEG.

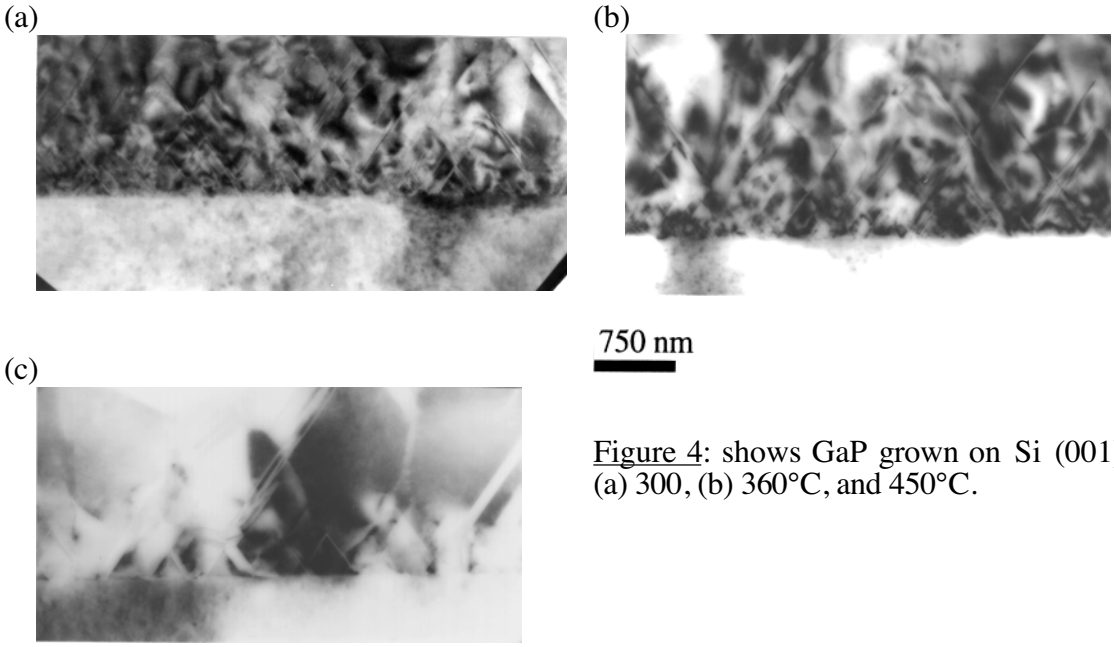


Figure 4: shows GaP grown on Si (001) at (a) 300, (b) 360°C, and 450°C.

Figure 4 shows a comparison of cross sectional transmission electron microscopy (XTEM) images of contiguous GaP films on Si(001) grown at (a) 350°C and (b) 380°C, and (c) 450°C under conditions of PCBE [2]. In all three cases formation of stacking faults and microtwins is observed, which occurs at all (111) variants, that is (111), $(\bar{1}11)$, $(\bar{1}\,\bar{1}1)$ and $(1\,\bar{1}1)$ - albeit at decreasing density with increasing temperature. We note that in Fig 4(c) stacking faults formed at opposite {111} facets terminate. This results in considerable improvement of the film quality. This can be further enhanced by the use of structured Si(001) surfaces composed of V-grooves that are produced by anisotropic etching along [110] or $[\bar{1}10]$ on the Si (001) surface selected by photolithographic patterning. An explanation for this has been given [1,7] in terms of dislocation reactions leading to formation of Lomer-Cottrell sessile dislocations that terminate propagation of the two interacting stacking faults. Here we propose an alternative route - based on observations made in overgrowth of patterned SiO_2-coated Si(001) wafers by GaP epilayers that suggest selection of just one variant in the overgrowth of slanted side faces of the SiO_2 mask. This is illustrated in Figure 5 where the growth of GaP on slanted side wall is more likely to have seeded from a single (111) variant of faceted nuclei that grown on an exposed silicon surface.

This selection process should permit the generation of GaP film that are free of stacking faults and microtwins upon epitaxial layer overgrowth (ELO) of the SiO_2 mask, as illustrated schematically in Figure 6(a). For comparison, an experimental result is shown in Fig. 6(b). Note that the SiO_2 film is not wetted by the GaP film as indicated by the re-entrant facet at angle β=45°. Based on the comparison of Figs. 4(a-c) an as high as possible substrate temperature is desirable in the ELO step. However, the process window unfortunately is limited to temperatures < 400°C since at higher temperatures the highly selective growth of silicon in the windows provided in the thermal oxide film is lost. This is illustrated in Fig. 7 that shows the nucleation of GaP on SiO_2-coated Si(001) resulting in the growth of polycrystalline ELO films. Further work is needed to test the extent to which ELO allows the suppression of planar defect propagation and to evaluate defect formation upon coalescence of ELO films emanating from neighboring windows in the thermal oxide

film. Preceding work on homoepitaxial ELO on Si substrates suggests that this is a problem [15] it may also be a problem in heteroepitaxial ELO and needs further study.

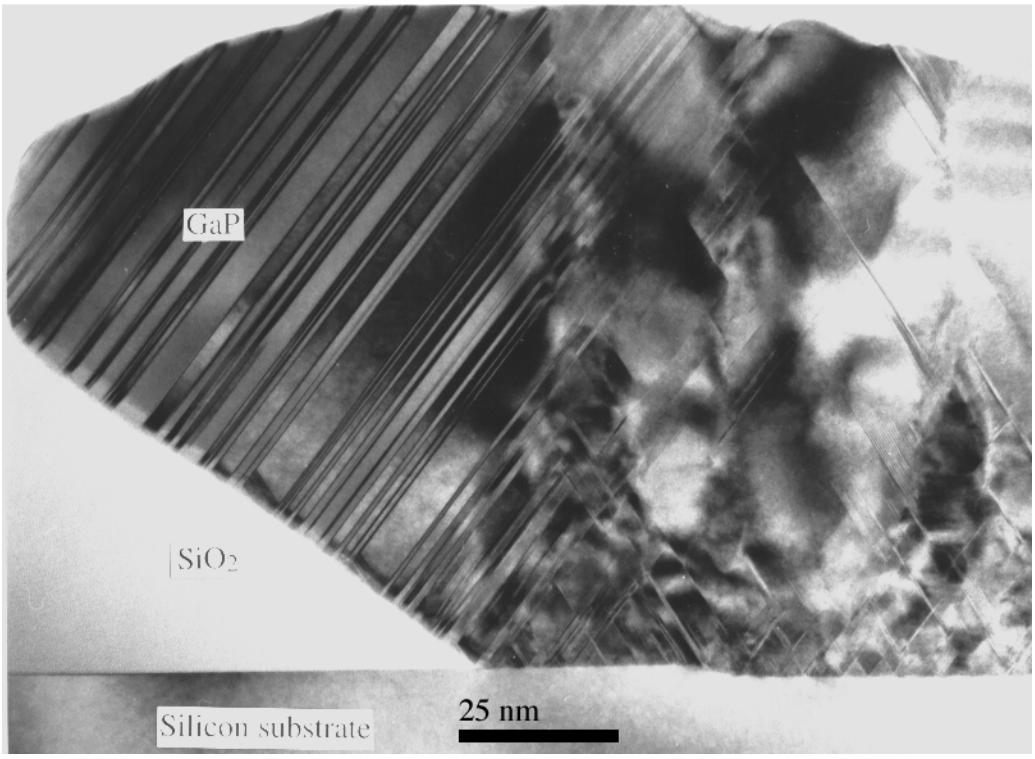
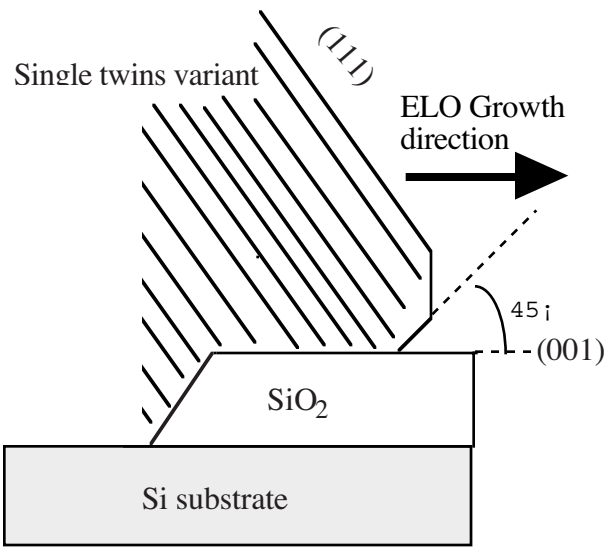
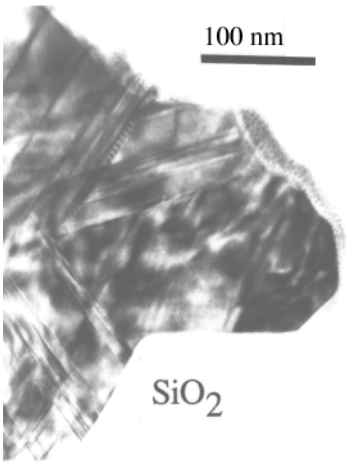


Figure 5: Shows GaP grown on slanted SiO_2 surface.

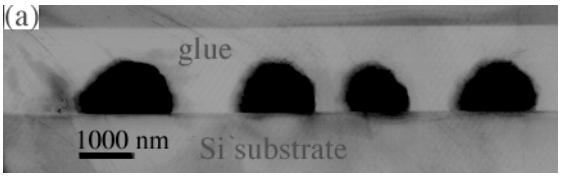


(a)



(b)

Figure 6: GaP overgrown on SiO_2 showing (a) facets on the overgrown layer and (b) schematic representation of expected single twinning variant.



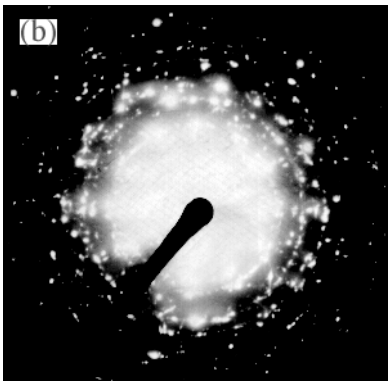


Figure 7: Shows the polycrystalline (a) film formed on SiO_2 coated Si (001) and corresponding SAD pattern (the thickness of the islands is 1000 nm)

SUMMARY

We described the selection of one twinning variant in the overgrowth of slanted side faces of windows in a thermal SiO_2 mask on a silicon (001) substrate wafer. We propose that this effect opens an opportunity for the fabrication of improved epitaxial films quality on Si(001) by epitaxial layer overgrowth (ELO). A more detailed evaluation of ELO of GaP films on SiO_2 coated Si(001) including the coalescence of ELO layers generated in neighboring windows is presently underway.

ACKNOWLEDGMENTS

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