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Journal of Crystal Growth 150 (1995) 691–695

JOURNAL OF CRYSTAL GROWTH

Migration-enhanced pulsed chemical beam epitaxy of GaP on Si(001)

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Abstract

In this paper, we present results on the heteroepitaxial growth of GaP on Si by migration enhanced pulsed chemical beam epitaxy (PCBE) using additional hydrogen and filament assisted techniques. For the real-time monitoring we applied a new technique, p-polarized reflectance spectroscopy (PRS) which provides information on the bulk, interface and surface properties of the grown GaP/Si heterostructures. The monitoring is initiated close to the Brewster angle for the substrate material, achieving high sensitivity in the initial phase of heteroepitaxial overgrowth. The bulk properties and growth rate are monitored using the quarter wave periodic structure in the reflectance based on interference in the film. The surface vicinity properties are monitored by the periodic fine structures in the intensity of the reflected light, which are correlated with the switching cycles of the metalorganic precursor pulses and are amplitude-modulated in accord with the repeat cycle of the heteroepitaxial growth process. Additional information regarding the surface roughness was revealed by scattered light measurements during the growth of the film. The results of real-time monitoring of nucleation and growth are combined with results of the ex-situ characterization of the GaP/Si heterostructure by cross-sectional transmission electron microscopy (TEM) and atomic force microscopy (AFM) studies to gain an understanding of the critical phase, in which the silicon surface becomes sealed by a contiguous epitaxial film of GaP. The defects formed in the GaP film during this phase determine the quality of the epilayers obtained upon prolonged growth.

Recently we have shown that epitaxial Si/GaP/Si double heterostructures can be grown around 300°C by a combination of chemical beam epitaxy (CBE) of GaP on Si(001) and remote plasma-enhanced chemical vapor deposition (RPCVD) of epitaxial Si on the GaP coated Si substrates [1]. Important interrelated aspects of PCBE of GaP on Si are the formation of defects in the early stages of nucleation and the incorporation of carbon in the growing epilayer. To address these problems, real-time monitoring of the epitaxial deposition process in the initial phase of nucleation and throughout the entire growth process is essential for the controlling of the growth process and the understanding of the growth mechanism. Methods such as reflection high energy electron diffraction (RHEED) [2], reflectance difference spectroscopy (RDS) [3] and surface absorption spectroscopy (SPA) [4,5] were developed to provide a better insight in the surface chemistry during the initial growth period.

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SSDI 0022-0248(94)00759-4

Their high accuracy, with resolution in the submonolayer region makes them powerful tools in the study of first monolayer of nucleation. However, these methods have been restricted to observations of the initial period of growth.

In contrast, PRS is developed as a real-time monitoring tool for heterostructural growth processes, which reveals real-time information of the interface/surface and bulk properties of the film over the entire growth process with high accuracy and without restriction to anisotropic surfaces. The PRS signal contains several components which can be divided into contributions from the bulk and the vicinity of the surface of the film. The contribution related to the heteroepitaxial growth of a film is described by the Fresnel equations for a three-layer system [6] (ambient/film/substrate) and can be easily extended to a multi-stack description. The changes in the amplitude of the reflectance due to growth of a GaP layer were predicted to be within two to three orders of magnitude with a quarter-wavelength periodicity of ~ 1050 Å for a He–Ne laser (6328 Å), assuming an angle of incidence of $\phi = 75.637°$ and dielectric constants of $\epsilon_{GaP} = (9.95, 0)$ and $\epsilon_{Si} = (15.25, 0.17)$ for GaP and Si, respectively. The changes in the amplitude of the reflected p-polarized light beam are strongly dependent on the differences in the dielectric functions of the film/multilayer stack and the underlying substrate. In the case of homoepitaxial film growth the bulk/film related contribution to the PRS signal vanishes, so that no information about the bulk properties of the growing film are available presupposing identical substrate and film properties with an ideal interface. Only the contribution to the PRS signal, that is related to the vicinity of the surface, is maintained throughout the entire film growth [7].

Fig. 1 shows the experimental setup for the real-time monitoring by PRS with integrated scattered light measurements and in-situ RHEED configuration. The system is built in a conventional ultra high vacuum CBE reactor chamber. The fluxes of triethylgallium (TEG), tertiarybutyl phosphine (TBP) and hydrogen are controlled by mass flow controllers and are directed over computer controlled 3-way valves to the reactor chamber or to a separately pumped bypass chamber [8]. For the PRS we used chopped polarized laser light (He–Ne laser, $\lambda = 6328$ Å), which irradiates the Si surface at an angle of incidence $\phi \approx 72°$ which is close to the Brewster angle of the substrate of $\approx 75.6°$. The light is parallel polarized to the plane of incidence using a Glan–Thompson prism with an extinction ratio better than 10^6 for the p-polarized component. The reflected light is detected by a Si photo diode with integrated preamplifier, whose output is fed through a lock-in amplifier and recorded in a data acquisition unit. Simultaneously, the reflected scattered light from the surface and from the interface is detected using a sensitive photo multiplier tube (PMT) whose output is routed to a second phase-sensitive amplifier and stored in the data acquisition unit. The real-time monitoring is synchronized with the switching sequence of the sources.

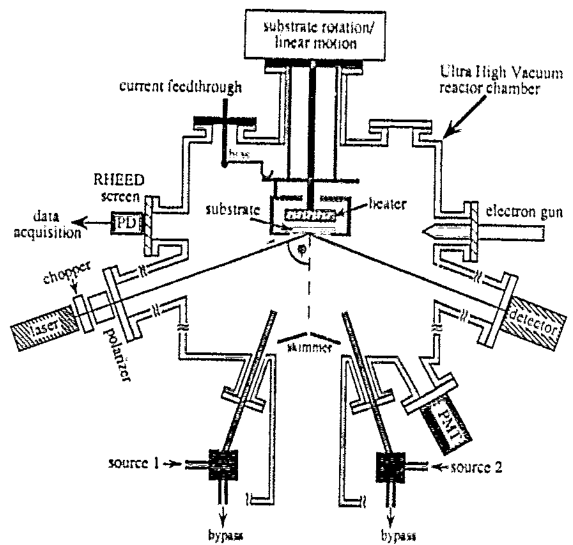

Fig. 1. Schematic representation of the PCBE reactor chamber with the experimental setup for PRS.

The PRS signal in Fig. 2 (upper curve with two enlargements) shows, as predicted, the quarter wavelength oscillation, which is used to terminate the growth of the film as soon as the reflected intensity reaches the second minimum. This corresponds to a film thickness of 1700 ± 50 Å. The error in the thickness is due to the lack of knowledge of the exact value of the angle of incidence,

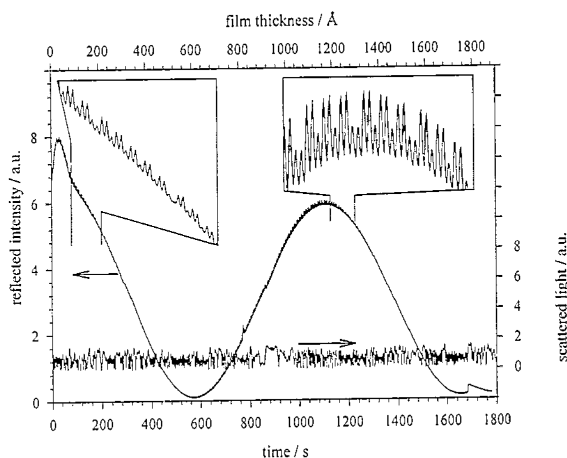

Fig. 2. PRS signal (upper curve with two enlarged inserts) and scattered light intensity (lower curve) for heteroepitaxial film growth of GaP on Si(001) at 310°C with a delay time of 2 s between the source pulses (total cycle time = 3 s).

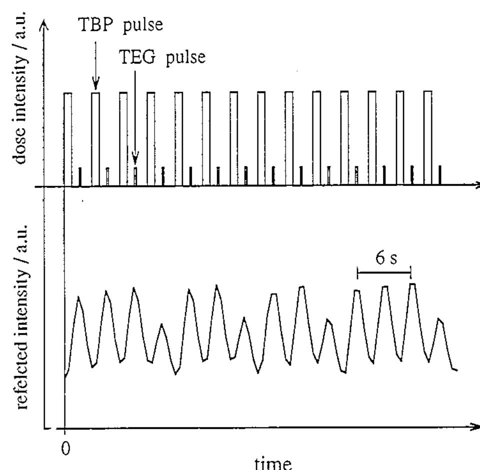

Fig. 3. TBP and TEG pulse sequence (top) with the corresponding oscillation in the PRS signal for 2 s delay time between the source pulses.

the change in the dielectric function of the substrate during the heat-up period to 310°C and the error in pinpointing the position of the second minimum, which relies at this time on a visual inspection of the signal. These errors can be eliminated by comparison of the experimental data with theoretical model calculations [9], which allows the computation of the optical constants of the film as well as the deviations in the dielectric function during the growth with an accurate prediction of the desired termination point of the growth process. The lower curve of Fig. 2 shows the intensity of the scattered light as a function of the growth time. In certain cases an increasing in the scattered light during the initial nucleation period can be observed, which can be related to the mechanisms of heteroepitaxial nucleation and initial overgrowth [7]. The inserts in the upper curve of Fig. 2 show enlarged sections of the amplitude modulated fine structure in the reflected intensity, which is maintained throughout the entire growth process. The periodicity of this fine structure and its amplitude modulation is strongly related to a complete cycle sequence and the growth rate per cycle, respectively. The cycle sequence for the GaP deposition is built-up by a TBP pulse of the length a followed by the delay x, a TEG pulse of the length b and a second delay of the length y. Fig. 3 shows the pulse sequence for TBP and TEG with $a:b = 0.8:0.2$ and a delay between the pulses of 2 s ($x:y = 0.8:1.2$). During the whole growth period a constant flow of hydrogen is introduced using a separate source inlet as well as through the TBP inlet port. A further reduction of the surface rough-

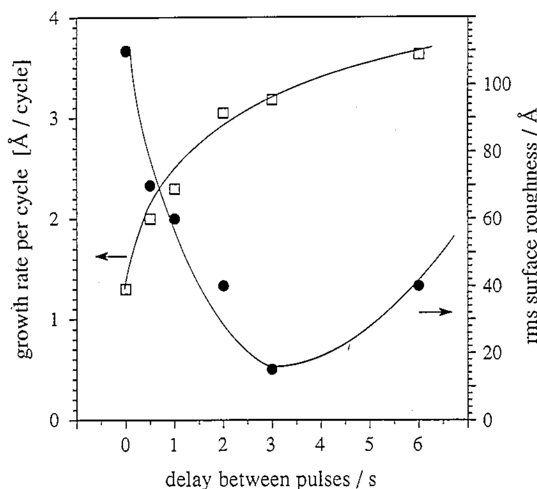

Fig. 4. Migration enhancement of the growth rate per cycle by varying the delay times between the source pulses with correlation of the observed RMS surface roughness of the heteroepitaxial grown GaP film on Si(001) at 310°C.

ness is achieved by inserting a heated filament in the hydrogen and/or TBP outlets.

The growth rate per cycle is calculated by multiplying the average growth rate, determined from the distance between adjacent minima that correspond to $\lambda/4$ in the film, with the time per cycle. At a specific fixed pulse width and height of the source vapors and a specific delay between pulses of 2 s, it is estimated to be 3.05 Å/cycle. The migration enhancement of the growth rate per cycle is shown in Fig. 4. With increasing delay time between a constant ratio of the source pulses, TBP:TEG ($a:b = 0.8:0.2$), the growth rate per cycle increases from 2 to ~3.6 Å/cycle for no delay and 6 s delay, respectively. The RMS surface roughness, measured by AFM, decreases rapidly with the increasing delay time and reaches a minimum at about 3 s delay time. A further increase in the delay results in an increase of the rms surface roughness and in an inhomogeneous film growth. Fig. 5 shows a cross-sectional HRTEM image of the GaP/Si interface and the grown GaP epilayer, indicating a well formed interface due to the close lattice matching for the GaP/Si heterostructure.

In conclusion, we have shown that PRS, as a real-time monitoring technique, can be applied to monitor the heteroepitaxial growth process of GaP on Si. PRS allows the measurement of the film thickness and the optical constants using the

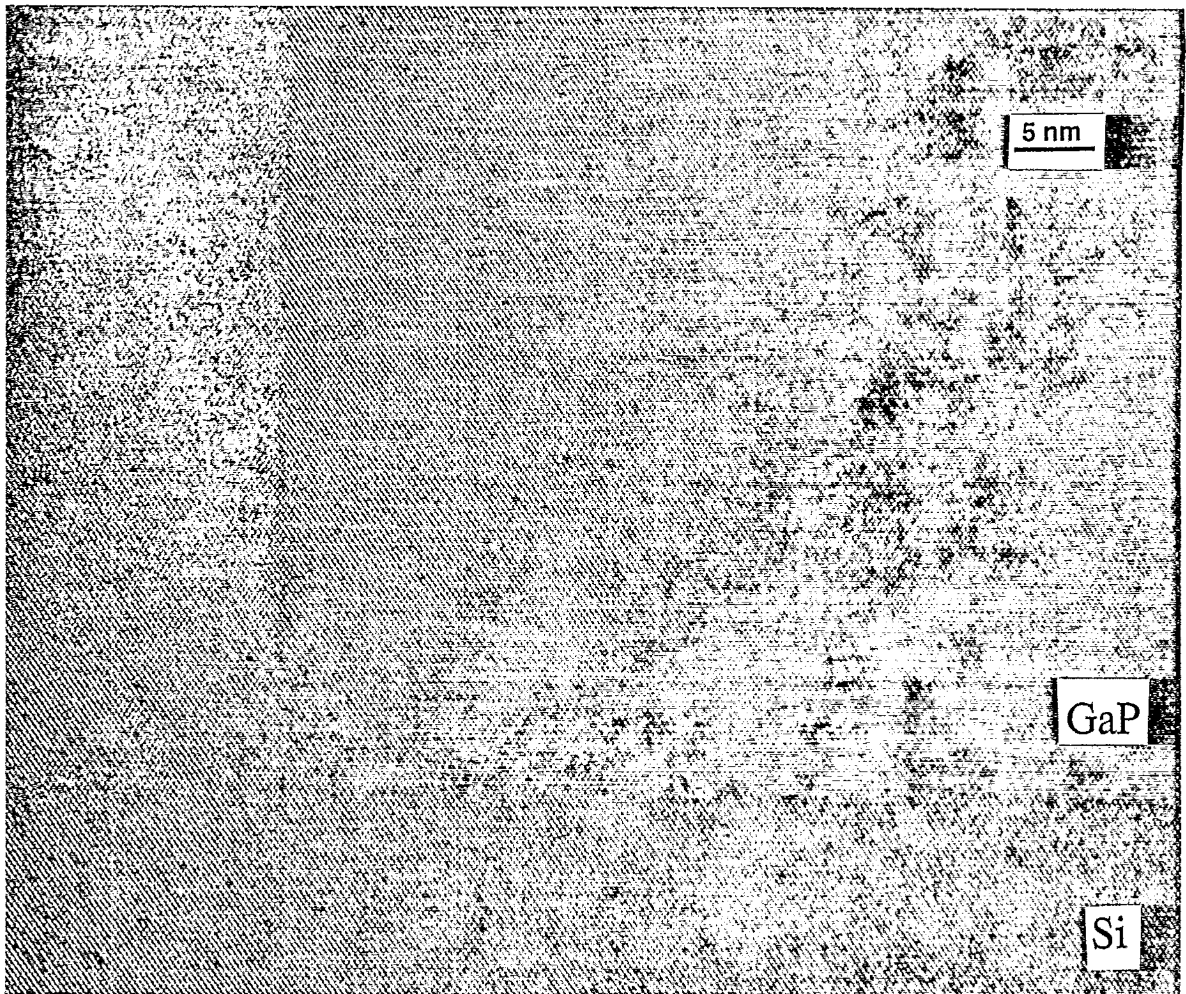

Fig. 5. Cross sectional HRTEM image of the GaP/Si interface and the GaP epilayer, grown on Si(001) at 310°C by PCBE.

quarter wave oscillation in the heteroepitaxial film growth process. The observed amplitude modulated fine structure provides an Å scale periodicity over the entire growth process and can be used for a better understanding of the surface chemistry during the deposition process. The oscillation, which builds up the amplitude modulated fine structure, may be modified using asymmetrical delay times between the source pulses. These variations reveal the contribution of each source pulse to the changes of the dielectric function in the vicinity of the surface.

This research is supported by the NSF grants DMR 9202210 and CDR 87211505.

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