Real-time Optical Monitoring of Epitaxial Growth Processes by p-Polarized Reflectance Spectroscopy

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ABSTRACT

In this paper we introduce a real-time optical probe technique, p-polarized reflectance spectroscopy (PRS), for the monitoring of epitaxial growth processes. GaP heteroepitaxy by pulsed chemical beam epitaxy (PCBE) is used as an example. PRS allows to follow the deposition process with submonolayer resolution, utilizing a fine structure that is superimposed to the interference oscillations in the reflected intensity. This fine structure is explained by the periodic alteration of the surface reaction chemistry under pulsed chemical precursor supply. In the case of epitaxial GaP growth, it is modeled for a four layer stack, including an ultra-thin surface reaction layer of periodically changing thickness $d_o(t)$ and dielectric function $\varepsilon_o(t)$ tied to the periodic surface exposure to tertiarybutyl phosphine (TBP) and triethylgallium (TEG) pulses, respectively. The imaginary part of the dielectric function, ε_{O2}, of this surface reaction layer can be determined directly from the distance of the inflection points in the fine structure, where the optical response to the first precursor pulse in the cycle sequence changes sign, from the closests interference minimum. The surface reaction kinetics can be studied by analyzing the decay time characteristic in the transients of the fine structure.

INTRODUCTION

The application of optical techniques to the real-time monitoring of deposition and etching processes is important for achieving a better understanding of surface reactions mechanisms in the engineering of thin layers with well defined optical and electrical properties. Various surface sensitive methods such as reflectance difference spectroscopy (RDS)[1] surface photo-absorption (SPA)[2] and spectral ellipsometry (SE)[3] have been developed. Recently, we added to these techniques, p-polarized reflectance spectroscopy (PRS), which combines a high sensitivity to surface reactions kinetics with the capability of monitoring film thickness and optical properties with submonolayer resolution[4-9].

PRS is based on a light beam that is parallel-polarized to the plane of incidence (p-polarized light beam) impinges the surface at the Brewster angle φ_B of the substrate, as schematically illustrated in fig. 1. On the silicon/vacuum interface the p-polarized reflectance component in the weak absorbent region ($\lambda > 500$ nm) is in the order of 10^{-4}. Therefore, the reflected intensity is a sensitive function of any changes in the dielectric function of silicon surface, which may be due to either temperature-induced changes in the dielectric function of the substrate, a surface coverage/roughening, chemical surface modifications or overgrowth by a thin film having a dielectric function that differs from that of the substrate. The former effect provides for real-time monitoring of temperature changes at the substrate surface and the latter effects provide for the real-time monitoring of surface adsorption and overgrowth processes. A simultaneous application of laser light scattering (LLS) measurement provides additional insight in the nucleation process and into the evolution of the surface morphology during the deposition process. In this paper we illustrate the capability of PRS on results obtained during homoepitaxial GaP growth and GaP heteroepitaxy on Si.

EXPERIMENT

To demonstrate the capability of PRS, we applied single-wavelength PRS during GaP heteroepitaxy on Si and GaP homoepitaxy under pulsed chemical beam epitaxy conditions. During the deposition process, the surface is sequential exposed to the precursors TEG [$Ga(C_2H_5)_3$], and TBP [$(C_4H_9)PH_2$] with an continuous flow of hydrogen in the background. A p-polarized light beam generated by a HeNe laser (λ=6328Å) and a Glan-Thompson prism

impinges on the substrate at an angle of incidence φ=72°, which can be adjusted in the range of 70°-75°and set with an accuracy of 0.01°. The reflected beam is detected by a Si photodiode and the intensity of the scattered radiation (LLS) is simultaneously monitored by a photo multiplier tube (PMT) located 45° from the plane of incidence. The switching of the sources is synchronized with the data acquisition of the PRS and LLS.

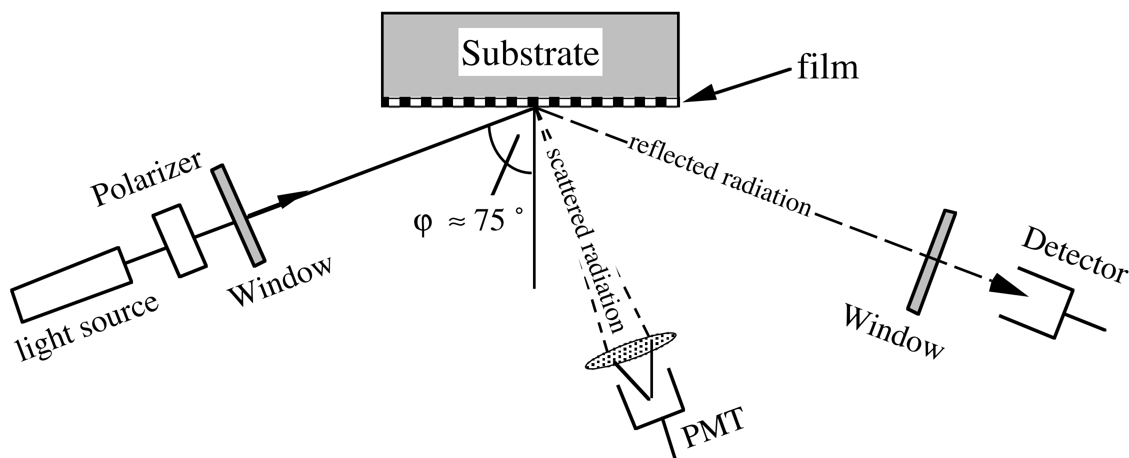


Figure 1. Schematic representation of the principle of PRS.

RESULTS

Figure 2 shows the time-evolution of the PRS and LLS signals during the growth of GaP on Si(001) at 350°C with a precursor cycle sequence time of 3 sec. Due to interference phenomena, minima and maxima are observed in the time evolution of the reflectivity as the film grows. Superimposed on the interference oscillations of the reflected intensity is a fine structure (see insert in fig. 2) that is strongly correlated to the timed sequence of the supply of precursors during the steady-state growth of GaP. Each peak in the fine structure represents a complete precursor cycle, consisting of a pulse of TBP, followed by a first delay period, a triethylgallium pulse, and a second delay period. In addition, an activated hydrogen beam impinges during the entire process onto the surface of the growing film. The fine structure thus relates to modifications of surface chemistry associated with the periodic exposure of the surface to the precursor pulses and a steady flux of hydrogen. Also shown (lower curve) is the change of the LLS intensity during the experiment. The evolution of the LLS and PRS signal during the initial growth period contains information about the nucleation process. For example, an increased PR signal during the initial growth period indicates an apparently larger difference in the dielectric functions between film and substrate than in the later stage of film growth. This can be explained by corrugations in the surface during the initial growth period, which requires the replacement of dielectric function for the bulk film by an effective dielectric function [5]. For large nuclei this three-dimensional nucleation period results also in an enhanced LLS signal. The extractable information from the evolution of the PRS and LLS signals during growth are analyzed in terms of the bulk and surface properties of the film as summarized in table 1.
In the case of homoepitaxy, the interference oscillations in the reflected intensity do not exist, but the fine structure persists, as illustrated in fig. 3 for one GaP PCBE experiments as example. Note that the fine structure in the homoepitaxy experiment exhibits an amplitude modulation and an additional envelope modulation at even lower frequency. These amplitude modulations are identical to those observed in heteroepitaxial experiments, indicating that growth information gained under heteroepitaxial conditions can be utilized to calibrate homoepitaxial growth [7].

In a simplified model, we assumed that the fine structure is caused by the presence of a periodically changed surface reaction layer $d_o(t)$ on top of the growing GaP film, which can be described by a four-layer (ambient / surface reaction layer / film / substrate) stack, as schematically shown in fig. 4. Fresnel's equations for a multilayer stack[5] were used to calculate the changes of the reflectivity for p-polarized light as a function of layer thickness, assuming homogenous isotropic media.

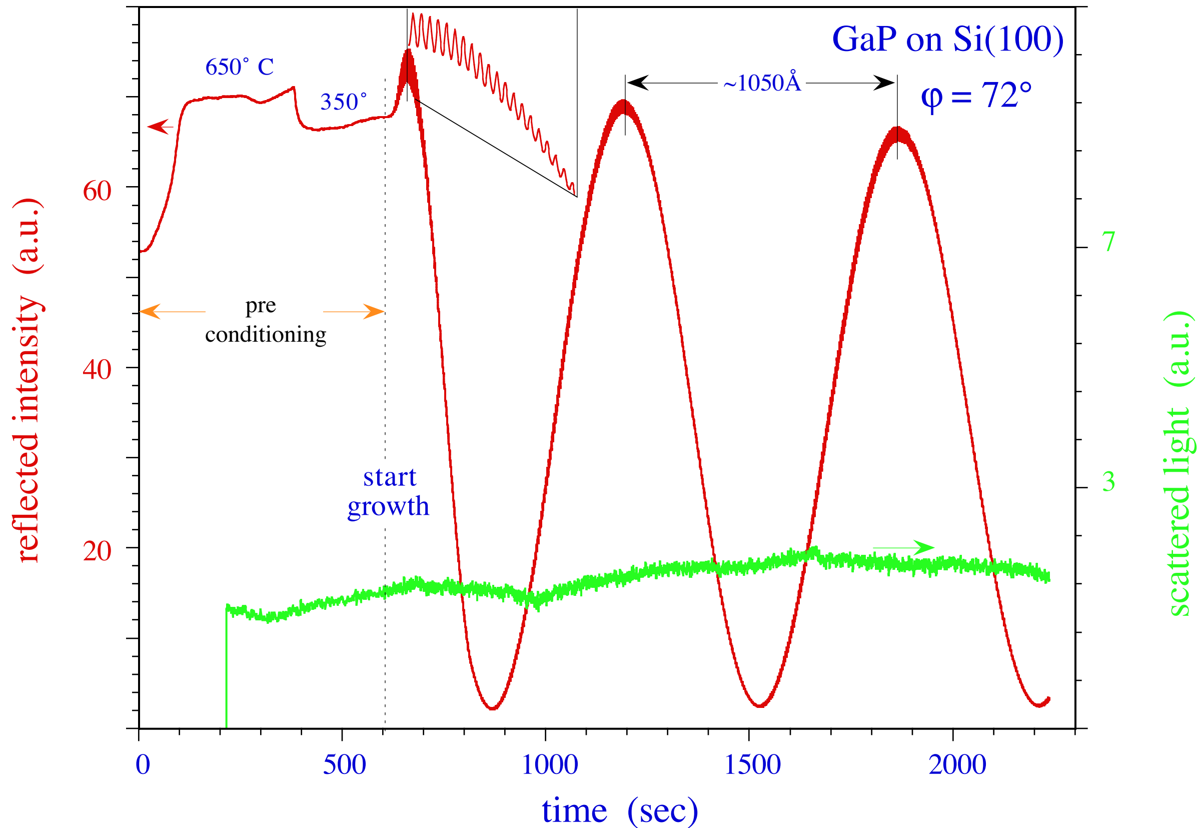


Figure 2. Interference Oscillation in the PRS signal vs. time traces observed during GaP heteroepitaxy on Si(001) under PCBE growth conditions at 350°C.

Observed feature	Related information
Changes in the reflected intensity during heat-up	Temperature dependence of the dielectric function of the substrate and surface conditioning
Spacing in the minima/maxima of the film interference oscillation	Growth rate
Amplitude of film interference oscillation	Dielectric function of film in relation to substrate
Excess structure in the PR signal during the initial nucleation period	Growth mechanism
Fine structure oscillations	Surface chemistry and kinetics
Locations of turning points of the fine structure with respect to the minima/maxima of the interference oscillations	Imaginary part of the dielectric function of the surface reaction layer
Bimodal envelope modulation of the fine structure	Surface reconstruction
Evolution of scattered light	Surface roughening / Interface perfection / Defect formation

Table 1: Characteristic Features in the PRS and LLS signals and related information

Figure 3.

Fine structure in the PRS signal for homoepitaxial GaP(001) growth by PCBE at 350°C.

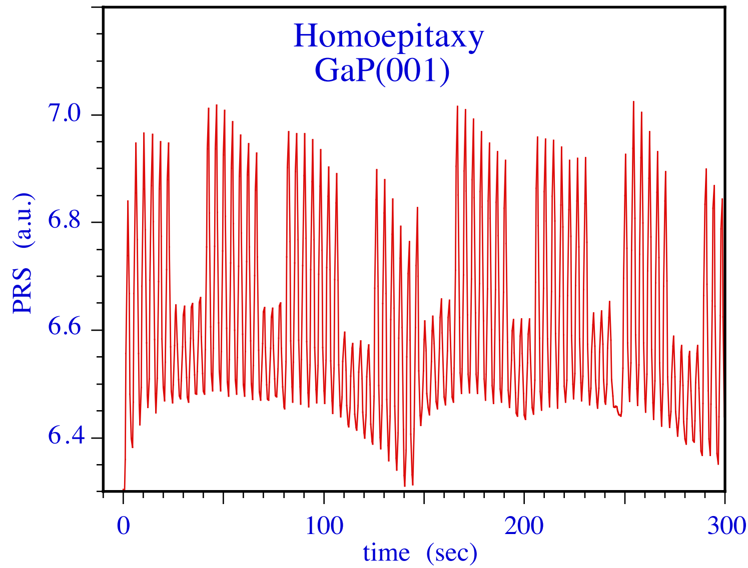
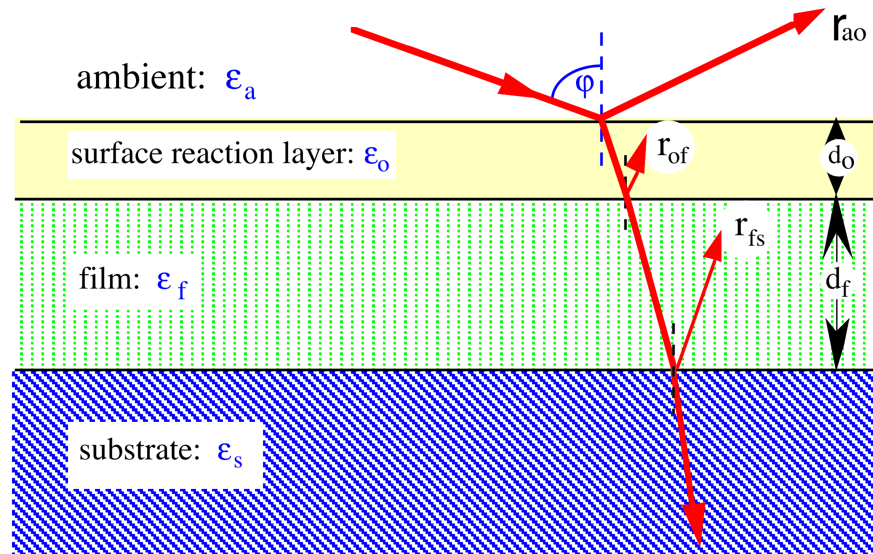


Figure 4.

Schematic representation of a four layer stack.



With these assumptions, the observed fine structure in the PRS signal is modeled by a periodically increased and decreased surface layer and the GaP film growth by the incorporation of products of the surface reaction layer in the growing bulk film[9]. Since the observed changes in the amplitude of the reflectance in PRS are a product of $d_o(t)$ and the differences in the dielectric functions of a surface reaction layer ε_o and the underlying film ε_f and the substrate ε_s, a more precise model has also to include periodic changes in the composition of the surface reaction layer during the subsequential precursor exposure of the surface.

The simulations of the effects of an additional surface reaction layer show that the imaginary part of the dielectric function, ε_{O2}, of such an ultra-thin layer is directly accessible from the inflection points in the fine structure. Figure 5 shows simulated data for GaP growth on Si assuming a periodic alternating surface coverage $d_o(t)$ during the subsequential TBP and TEG exposure of the surface with a maximum surface coverage of 3Å. If no absorptivity in the surface reaction layer is assumed, the inflection point coincide with the minima and maxima of theinterference oscillation. With increasing absorptivity (ε_{O2}>0) in the surface reaction layer and a refractive index lower the that of the bulk film (ε_{O1}<ε_{f1}), the position of inflection shifts downwards to a smaller film thickness. With a refractive index higher than that of the bulk film (ε_{O1}>ε_{f1}), the position of inflection shifts upwards to a larger film thickness. The evaluation of

the position of the inflection point allow therefore a direct access to the absorptivity of a ultra-thin surface reaction layer. A more detailed description is given in reference [9].

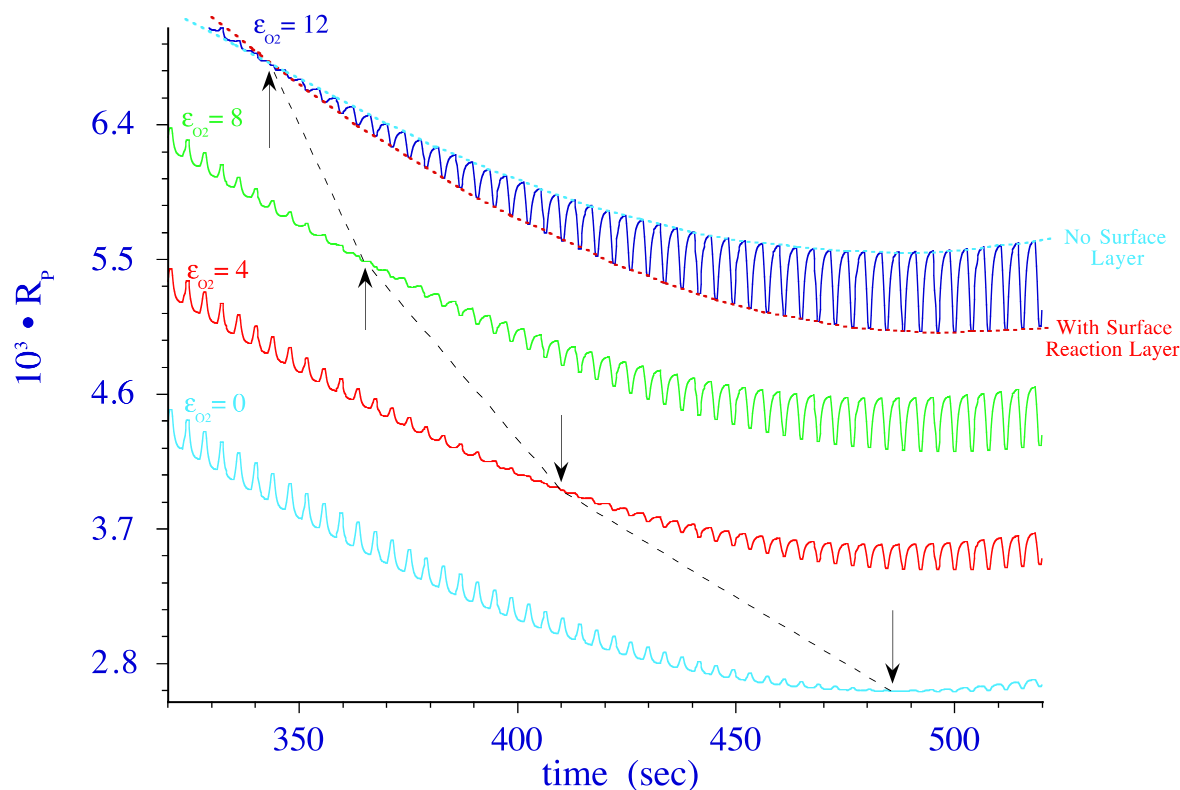


Figure 5. Shift of the inflection points in the fine structure due to absorptivity, ε_{O2}, in the surface reaction layer with ε_{O1}=6.0, ε_{GaP}=(11.11, 0.0), ε_{Si}=(15.25, 0.17), λ=632.8nm and a growth rate of 4Å/s.

For more specific information about the time constants of the surface-reaction kinetics, we performed experiments with single pulses of TEG and TBP. As an example, the PRS and LLS responses to individual precursor pulses for a double-pulse experiment, consisting of double TEG and TBP pulses on the raising flank of the PR interference oscillation are shown in fig. 6. The experiments are performed under quasi steady-state GaP growth conditions during an interruption of growth. After a 0.5 sec exposure of the surface to TEG, the TEG fragments decompose on the surface resulting in an increase in the PRS signal and a delayed increase in the LLS intensity, which is related to the Ga cluster formation. After the second TEG pulse the PRS signal increases as a response to an increased surface reaction layer, but stays constant during the further waiting period. The slight decrease of the PRS signal during the waiting period after the first TEG pulse can be related to the partial reaction of the TEG fragments with remaining phosphorus on the surface, which reduces the thickness of the surface reaction layer. This decrease is not observed after the second TEG pulse. The optical response to the first TBP pulse is significant. First, the PRS signal decreases exponentially and levels off at a slightly increased reflectance baseline due to the increase of the GaP film thickness. Secondly, the LLS intensity decreases slowly indicating a smoothing of the GaP surface. For the second TBP exposure no further changes in the PRS signal are observed.

CONCLUSION

PRS is a highly sensitive optical real-time monitoring technique that is readily applicable to hetero- and homoepitaxial growth processes, such as, GaP growth on Si and GaP substrates,

respectively. PRS allows precise measurements of the film thickness and the optical constants. The high surface sensitivity of this method permits the observation of a fine structure, which provides an Å scale periodicity over thousands of Å of film growth. Although the interference oscillations associated with heteroepitaxial film growth are lost under the condition of homo-epitaxial growth, the fine structure is maintained, allowing the real-time assessment of the growth rate in homoepitaxial processes. The high surface sensitivity of PRS also allows to follow changes in a ultra-thin surface reaction layer, which can be utilized for a better understanding of surface reaction kinetics and topography under steady-state growth conditions.

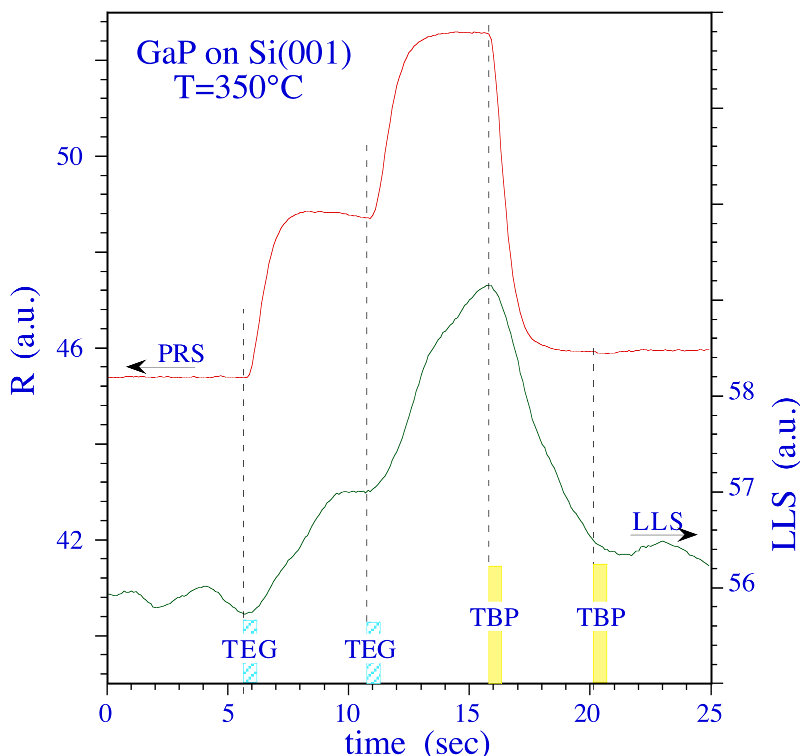


Figure 6.

PRS and LLS responses to individual precursor pulses performed during an interruption of growth at growth temperature.

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