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Applied Surface Science 102 (1996) 47–51

applied
surface science

Real-time optical monitoring of heteroepitaxial growth processes on Si under pulsed chemical beam epitaxy conditions

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Abstract

For an understanding of the surface chemistry and defect formation during the initial nucleation period and heteroepitaxial overgrowth process, real-time methods with sub-monolayer resolution are essential. We present results of a combined study of p-polarized reflectance (PRS), reflectance difference spectroscopy (RDS), and laser light scattering (LLS) during the growth of GaP on Si by pulsed chemical beam epitaxy (PCBE) with tertiarybutylphosphine, triethylgallium, and trimethylindium precursors. The pulsed supply of chemical precursors causes a periodic alteration of a surface reaction layer, which is observed as periodic fine structure in the PR and RD transients. This fine structure is used to study the nucleation and overgrowth process with submonolayer resolution. Both, PRS and RDS, show changes in the initial nucleation period, which are related to the three-dimensional nucleation process. The surface reaction kinetics for the precursors is studied under quasi-steady-state growth conditions.

1. Introduction

The formation of defects during the initial stage of nucleation and overgrowth is a major problem of heteroepitaxy that limits the performance and reliability of heterostructure devices and circuits. For example, in spite of strong technological motivations for the integration of silicon technology and compound–semiconductor optoelectronics (e.g., in the context of optically interconnected common memory and integrated sensor functions), device-quality compound–semiconductor heterostructures on silicon have not been realized because of the massive forma-

tion of defects during the heteroepitaxial overgrowth. To gain insight into the mechanisms of defect formation in the initial stage of nucleation and overgrowth, the application of nondestructive real-time optical techniques is attractive for monitoring of deposition processes. Industrial applications have included monitoring growth rates and composition with spectral resolved normal incidence reflectance spectroscopy (NRIS) [1] and pyrometric interferometry (PI) [2] and the control of growth with spectroellipsometry [3,4]. To gain a higher sensitivity to surface- and interface-related growth properties, surface-specific in-situ optical observation methods such as reflection difference spectroscopy (RDS) [5,6] and surface photo absorption (SPA) [7,8] have been developed. Recently, we added p-polarized reflectance spectroscopy (PRS) to these techniques [9–16]. PRS

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achieves both (i) high sensitivity to surface kinetics processes under steady-state growth conditions and (ii) a capability of monitoring of film thicknesses and optical properties with submonolayer resolution. PRS measures the reflectance $R_p = r_p r_p^*$ of p-polarized light at or near the Brewster angle φ_B (pseudo-Brewster angle for an absorbent media) of the substrate. To probe for both surface and film properties, PRS is applied in the transparent or weakly absorbent wavelength range of the growing film. Here the reflected intensity is a sensitive function of any changes in the dielectric response of the sample, which may be a temperature-induced change in the dielectric function of the substrate, a chemical modification or roughening of the surface, or an overgrowth by a thin film having a dielectric function that differs from that of the substrate.

In this work we describe the application of single-wavelength PRS and laser light scattering (LLS), $\lambda = 6328 \text{ \AA}$, to monitor and characterize the heteroepitaxial nucleation and overgrowth process of GaP on Si. The nonspecularly scattered intensity is detected by a photomultiplier tube (PMT) located 45° from the plane of incidence. We simultaneously applied RDS to measure the optical anisotropy of the sample, which is normally determined by the differences in the reflectance for light linear polarized along the $[-110]$ and $[110]$ principal axes of the (001) surface. The configuration and approach have been described in detail elsewhere [6]. The RDS spectral range is 1.5 to 5.5 eV. The light enters the chamber through a nominally strain-free quartz window [17].

PRS, RDS, and LLS data are obtained simultaneously 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 tertiarybutylphosphine (TBP, $(C_4H_9)PH_2$) and triethylgallium (TEG, $Ga(C_2H_5)_3$) at typically 350–400°C to accomplish nucleation and overgrowth of the silicon substrate by an epitaxial GaP film. Two orientations were used: vicinal Si(001) substrates, cut 6° toward (011) and Si(113). Both were boron-doped with resistivities from 1 to 10 Ω cm. The wafers were given an RCA clean followed by a DI- H_2O rinse, a final HF dip, and a short DI- H_2O rinse before being transferred via a load lock into the growth chamber. This treatment pro-

duces a (1×1) hydrogen-terminated surface on Si (001) as verified by RHEED. The fluxes of the precursor and hydrogen are established by mass flow controllers and are directed via computer-controlled 3-way valves to either the reactor chamber or a separately pumped bypass chamber. This allows the sequential exposure of the substrate to individual pulses of the precursor molecules. 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 epitaxial film. Typical growth rates under the chosen pulsed chemical beam epitaxy (PCBE) growth conditions are in the order of 1 $\text{\AA}/s$. Further details on the experimental conditions are given in a previous publication [13].

2. Results and discussion

Upon heteroepitaxial growth of GaP on Si, the time-evolution of the PRS reflectance $R_p = r_p r_p^*$ shows an interference oscillation due to the increasing thickness of the film. Under the pulsed precursor conditions a fine structure in the PR and RD response is observed, which is linked directly to the precursor cycle sequence and therefore of surface origin. From a measurement of the separation between adjacent extrema in the interference oscillation, a determination of the number of precursor cycles/fine structure maxima between these extrema, and knowledge of the dielectric function of GaP at the laser wavelength, the thickness deposited per precursor cycle can be calculated for quasi-steady-state growth conditions [13]. The characteristic features in the PR and LLS signals during the nucleation and overgrowth period of GaP on Si are shown in Fig. 1. In Fig. 1(a), both signals show an increase during the first 6 precursor cycles (24 s) of GaP growth on a Si(001) 6° substrate, which indicates island formation. The decrease in the LLS signal after this nucleation period indicates a smoothing of the surface by overgrowth of the initially formed nuclei. During further growth, the LLS signal increases steadily, indicating an increas-

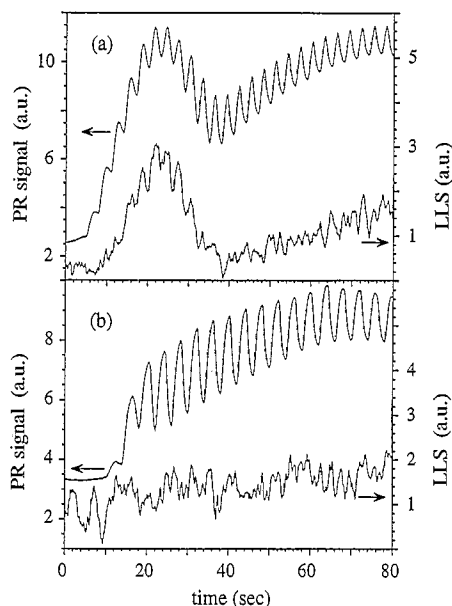


Fig. 1. (a) PR and LLS signals during nucleation and overgrowth of GaP on Si. (b) PRS and LLS signals during nucleation of GaP on Si by increased TEG flux during the first 6 precursor cycles.

ing in the surface roughening. The layer cannot be recovered. The behavior in the PR signal during the nucleation period is a result of the fact that the effective dielectric function of the film is more different from that of the substrate at incomplete coverage than after the film becomes contiguous [14]. This can be described in the Maxwell Garnett effective medium theory as

$$\varepsilon_{\text{eff}} = \varepsilon_a \frac{\varepsilon_f(1 + 2f_g) + 2\varepsilon_a(1 - f_g)}{\varepsilon_f(1 - f_g) + \varepsilon_a(2 + f_g)} \quad (1)$$

where the volume fraction f_g of GaP varies between $0 \leq f_g \leq 1$ [14]. During partial coverage the effective dielectric function is smaller than that of the contiguous film, resulting in a higher reflectance during the nucleation stage under the assumption of a constant thickness. For rough surfaces, the correlation of the enhancement of the PR intensity to the corrugation depth, as established by ex-situ AFM studies [10,11] can be used to monitor changes in the nucleation and overgrowth kinetics from three-dimensional toward a more two-dimensional behavior upon changing the supersaturation at the surface. Fig. 1(b) shows GaP growth on a Si(113) surface with a slightly in-

creased Ga-precursor flux during the initial period of nucleation. Here, we see no excess PR or LLS signals, which can be related to both the increase of the density and reduction of the height of the nuclei as a result of gallium supersaturation as well as the more uniform catalytic decomposition of *t*-butPH₂ by surface gallium.

Fig. 2 shows the PR, RD, and LLS responses for GaP nucleation on a 6° vicinal Si(001) substrate. The excess in the PR signal during the first few precursor cycles is strongly reduced due to the increased TEG flow during the first 20 s of growth. No significant increase in the LLS signal is observed. The evolution of the RD transient, monitored at 2.6 eV, shows a minimum in the early stage of the heteroepitaxy, which can be attributed to the formation of asymmetric islands. The islands coalesce to form a continuous layer of effectively reduced roughness, resulting in the RD baseline returning to zero. The RD signal is overlaid by a fine structure that is correlated to the precursor cycle sequence. The baseline behavior supports the suggestion of higher nucleation density of smaller nuclei with increasing Ga supersaturation that is not observable in the LLS signal in Fig. 2(b).

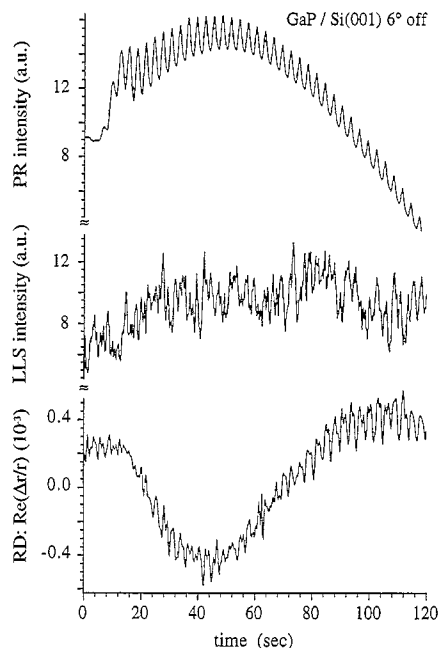


Fig. 2. RD, PR, and LLS signals during nucleation and overgrowth of GaP on 6° vicinal Si with increased TEG flux during the first 5 precursor cycles.

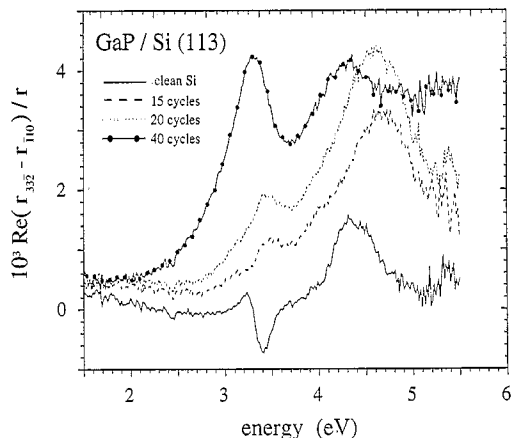


Fig. 3. Evolution of RDS spectra during GaP growth. The sample labeled clean Si is taken with the sample at room temperature; the rest are obtained at 350°C. Both substrate and the GaP layer usually show negative values in the RD spectrum. For the sake of clarity the sign was therefore switched.

Fig. 3 shows RD spectra taken during interrupted periods during the otherwise continuous growth of GaP on Si(113). For these spectra the substrate was kept at the growth temperature under continuous TBP flow. For comparison the room-temperature (RT) spectrum of the clean Si(113) surface is shown at the bottom. Unlike the case of vicinal Si(001) the sign of the substrate signal is opposite to that of the layer. Two notable features develop in the spectra. A structure initially at 3.4 eV shifts to 3.3 eV and becomes much stronger. Second, a structure near 4.6 eV for small coverages shifts to 4.3 eV at high coverages. The last spectrum, which is observed after 40 cycles, is a dielectric-function-type of RD spectrum as discussed in detail in [18]. At the earliest stages an assignment of the signal exclusively to the GaP layer is not possible, because the GaP/Si interface may still contribute. The similarity in spectral position of the 3.4 eV features in the original and 15 cycle spectra suggest that this is the case.

2.1. Surface reaction kinetics under quasi-steady-state growth conditions

For a more detailed understanding of surface reaction kinetics, experiments involving single pulses of TEG and TBP were performed under quasi-steady-state GaP growth conditions during an interruption in

growth. Fig. 4 shows the PR and LLS transients during individual pulses of the precursor TEG and TBP, observed on a falling flank of the underlying PR interference oscillation. After exposure of the surface to TEG for 0.5 s, the PR signal decreases. The LLS transient increases with a slight delay with respect to the PR response. During the 15 s waiting period the LLS intensity remains at the same level, while the PR signal reverts with a decay time of a few tens of seconds. The following TBP pulse resets the PR signal, except for a small shift due to the increased GaP layer thickness. The evolution of the PR signal during the waiting period is correlated with a decrease of scattered intensity, indicating the existence of chemical reactions that contribute to surface smoothing. A repeat of the single TEG–TBP pulse sequence with a 20 s waiting period shows qualitatively similar results, but in the following waiting period the LLS signal increases. After a series of such single pulse experiments the overall scattered light increases significantly. If a second TBP pulse is given after a 40 s waiting period, the second pulse has no effect in the LLS trace but results in a small increase in the PR transient. This indicates either a slow TBP fragmentation or a partial decomposition of phosphorous on the surface. These experiments show that TEG fragments have the tendency to cluster, but that the clusters are smoothed out after exposure to TBP. This behavior agrees with the observation of three-dimensional nucleation and overgrowth on silicon [10,11].

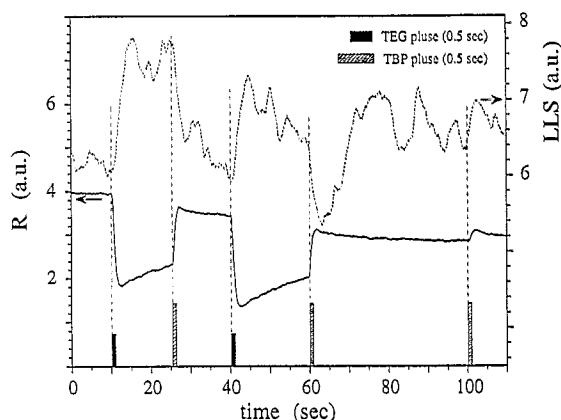


Fig. 4. PRS and LLS responses to individual precursor pulses performed during an interruption of growth at growth temperature with molecular hydrogen present.

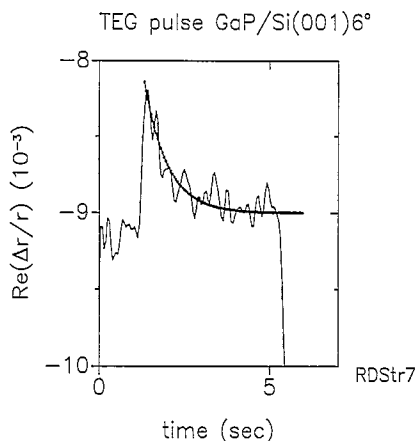


Fig. 5. RD transient at 3.6 eV during a single pulse TEG and a single TBP pulse at 5 s. The dash-dotted line represents the calculated transient with a decay time of 0.69 s.

Fig. 5 shows the RD transient for a single TEG pulse of 0.5 s duration with molecular hydrogen present. With the rising edge of the TEG pulse the RD signal increases linearly. After the pulse, the RD transient decreases exponentially with a decay time determined to be 0.69 s.

The observed response in experiments involving single TEG and TBP pulses is in good agreement with the four layer stack model [16], which describes the fine structure as a result of a surface reaction layer that is periodically generated and consumed during PCBE growth conditions. This causes a corresponding periodic alteration of the optical response, which can be described in the three-(ambient/film/substrate) and four layer (ambient/surface reaction layer/film/substrate) phase model.

3. Conclusion

We have monitored the nucleation and overgrowth of GaP on Si in real-time with RDS, PRS, and LLS and have shown that these approaches yield complementary information leading to a better understanding of surface reaction kinetics. An increased TEG flux during the initial period of nucleation results in an increased density of smaller nuclei, which decreases the amount of scattered light but still contributes to the initial surface roughening

as revealed by RDS. Single-precursor-pulse experiments under quasi-steady-state growth show that both RDS and PRS are sensitive to small changes of the surface reaction layer and are therefore suitable for revealing the surface reaction kinetics of growth processes.

Acknowledgements

This work is supported by the Alexander von Humboldt Foundation, the Office of Naval Research under contract N-00014-93-1-0255, and ARPA/AFOSR Grant F496209510437.

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