Real-time monitoring of homoepitaxial and heteroepitaxial processes by *p*-polarized reflectance spectroscopy

N. Dietz and A. Miller
Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7919

K. J. Bachmann
Department of Materials Science and Engineering and Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7919

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In this communication we describe a simple, inexpensive technique for the real-time monitoring of epitaxial processes based on the reflection of a parallel-polarized light that impinges onto the surface of the substrate close to the Brewster angle for the substrate material. In the case of heteroepitaxy, a quarter-wavelength modulation of the intensity of the reflected light is observed, which contains information concerning the evolution of the optical properties as well as a record of the growth rate for the entire duration of film deposition. Changes in the amplitude of this signal provides information about deviations in bulk dielectric properties of the growing film caused by absorption and inhomogeneities in the refractive index of the film as well as changes in the surface roughness. Furthermore, under the conditions of pulsed chemical beam epitaxy (PCBE), the reflected intensity contains a periodic oscillation that is superimposed on the polarized reflectance spectroscopy (PRS) signal with an Å scale period and is maintained over thousands of Å of film growth. The periodicity of this fine structure matches the period of the sequence of precursor pulses of the PCBE process. Also, an amplitude modulation of the superimposed oscillation is observed which may be understood on the basis of the results of PRS studies of homoepitaxial growth. Under the conditions of homoepitaxy, the quarter-wavelength oscillations in the PRS signal cease to exist since the epitaxial film and the substrate have the same dielectric function. However, the fine structure can still be observed and may be utilized for both analysis of the growth mechanism and in conjunction with the observation of heteroepitaxial growth for the same material, the real-time monitoring of the growth rate.

Figure 1 shows a schematic representation of the experimental arrangement for the specific conditions of pulsed chemical beam epitaxy (PCBE). Ballistic beams of the precursors to growth are combined on the surface of the substrate wafer, which is radiatively heated from its backside. Here we use GaP epitaxy on Si(001) and GaP(001) substrates as examples of heteroepitaxial and the homoepitaxial growth. Tertiary-butylphosphine (TBP) and triethylgallium (TEG) beams are employed as source materials and the substrate temperature is chosen in the range $300 \leq T_s < 350$ °C. The source vapor flows are selected and monitored by mass flow controllers and are switched between the growth chamber and a separately pumped bypass chamber to result in a sequential exposure of the substrate to individual pulses of the precursor molecules. In addition, the surface of the epitaxial film is exposed to a continuous beam of hydrogen that scavenges organic molecules formed on the surface of the epilayer due to the pyrolysis of the TBP and TEG molecules.[1]

For the real-time monitoring of GaP growth we use the combination of a HeNe laser with a Glan–Thompson polarizer, generating a *p*-polarized light beam of 632.8 nm that impinges onto the surface of the substrate near to the Brewster angle (~75° for Si at room temperature). The reflected signal is detected by a Si photodiode and is processed through a phase-sensitive amplifier and read into a computer. Upon heteroepitaxial film growth the intensity of the signal oscillates at quarter-wavelength intervals between adjacent minima as illustrated in Fig. 2, where minima in the reflected intensity are observed after 750 and 2100 s. Since upon heating of the substrate the Brewster angle position changes due to the temperature dependence of the dielectric function, the reflected intensity does not start in a reflectance minimum and, upon initiation of heteroepitaxy, the subsequent minima at a quarter-wavelength distance from each other occur at non-zero residual reflectance. These effects can be computed

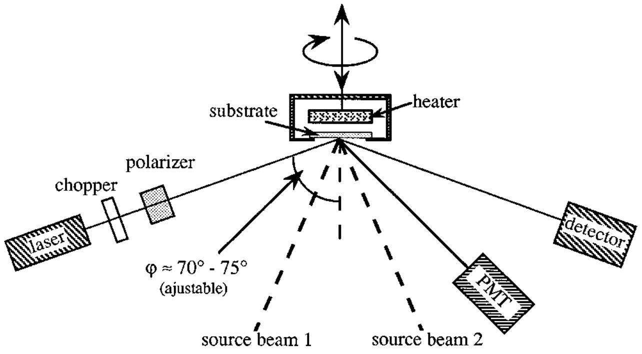

FIG. 1. Schematic representation of the experimental arrangement of PRS under the conditions of PCBE.

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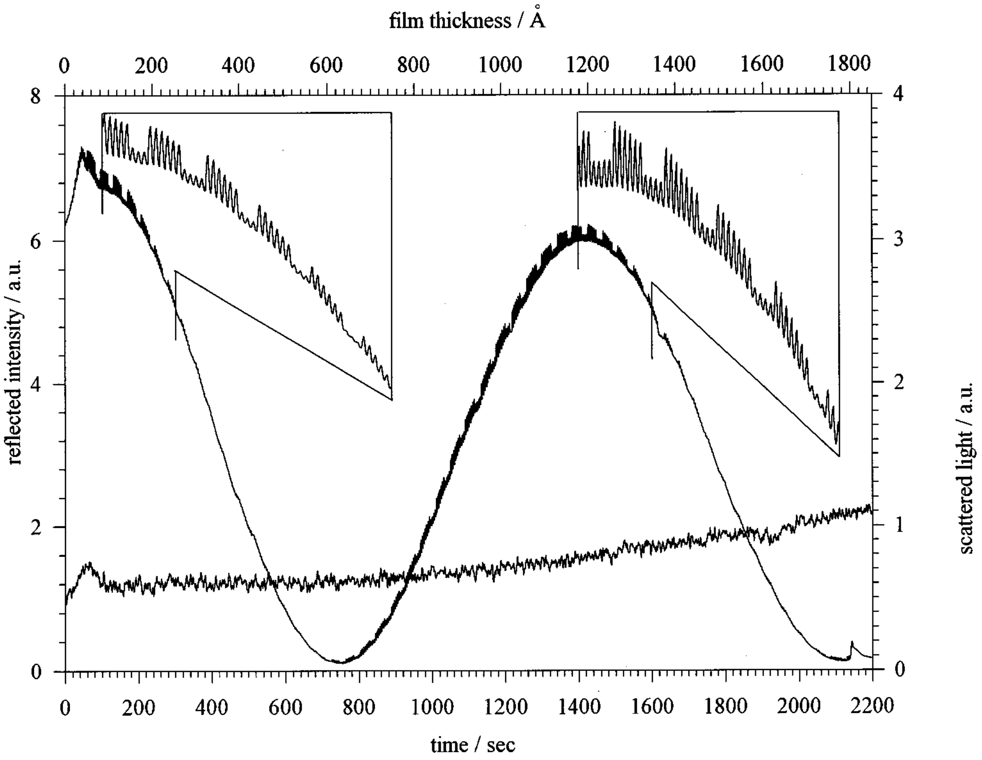

FIG. 2. PRS signal and scattered light intensity for heteroepitaxial growth of GaP on Si(001) at 310 °C.

for any specific materials combination for which the dielectric properties are known.[2]

The intensity of the maxima in the polarized reflectance spectroscopy (PRS) signal is determined by absorption in the film and by scattering of the laser beam at its surface. Since absorption also affects the residual reflectance at the position of the minima in the PRS signal, which in the experiment depicted in Fig. 2 does not change significantly, the reduction of the intensity between adjacent maxima shown in Fig. 2 is primarily caused by scattering. This is in accord with the observation of increasing intensity of the associated scattered light (bottom trace in Fig. 2) with increasing growth time/film thickness. The scattered light intensity is measured by a photomultiplier tube positioned outside the path of the reflected beam (see Fig. 1). Note that, at the onset of heteroepitaxial growth, a peak is observed in the scattered light intensity trace which provides information on the initial nucleation and overgrowth phase of the heteroepitaxial process.

An amplitude-modulated periodic fine structure on the reflected intensity that is particularly pronounced on the rising slope and maxima of the quarter-wavelength modulated signal is maintained over the entire duration of film growth. The periods of this fine structure and of its amplitude modulation do not change between adjacent maxima at quarter-wavelength distance, as illustrated in the expanded insets in Fig. 2. Each peak in the fine structure corresponds to a specific cycle of the precursor sequence that starts with a TBP pulse and is followed by a pause of fixed duration, a TEG pulse and a second pause of another fixed duration. This is illustrated in Fig. 3 for the pulse sequence used in a GaP homoepitaxy experiment. Under the conditions of GaP homoepitaxy, the quarter-wavelength modulation vanishes because of the absence of interference in the homoepitaxial film, but the fine structure that is related to the changes in the optical properties in the vicinity of the surface is maintained. This effect can be modeled assuming a very thin surface layer with a dielectric function that differs from the underlying film, thus extending the model to a multilayer stack,

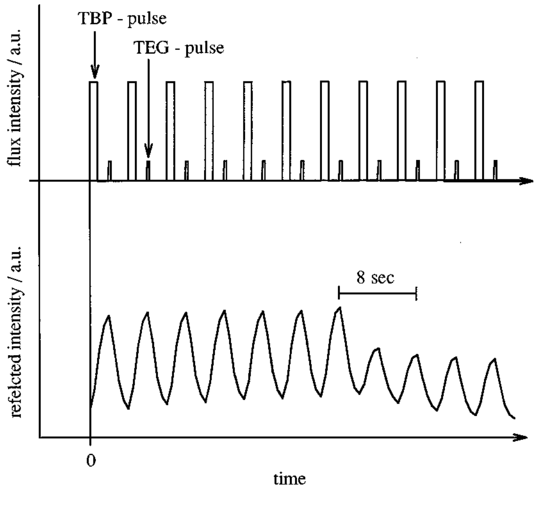

FIG. 3. TBP and TEG pulse sequences (top) and amplitude-modulated PRS signal for homoepitaxial growth of GaP on GaP(001) at 310 °C.

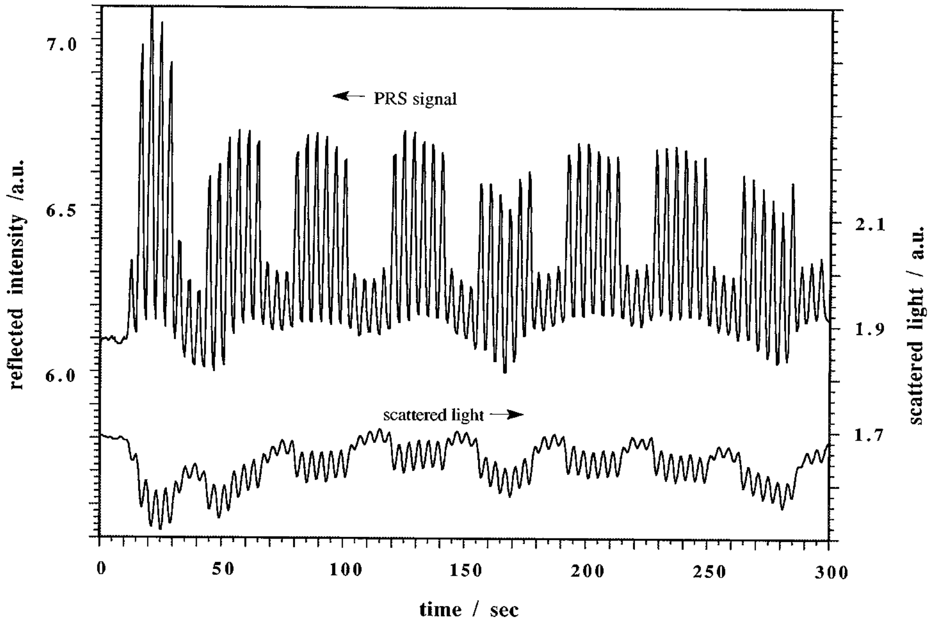

FIG. 4. Correlated amplitude modulation of the periodic PRS and scattered light intensities in the initial phase of homoepitaxial growth of GaP on GaP(001) at 310 °C.

which will be described in more detail elsewhere.[13] The phenomenon of surface absorption spectroscopy reported for the homoepitaxial growth of GaAs by molecular beam epitaxy[14] thus represents a special case of PRS.

Figure 4 shows the PRS signal and the scattered light signal for the initial stage of GaP homoepitaxy on a GaP (001) substrate wafer. Both the PRS and the scattered light signals show amplitude modulations that are correlated, indicating that the amplitude in the fine structure is related to cyclic changes in the surface structure at a scale that is commensurate with the scattering process. The details of this cyclic process are presently not understood and require further research.

[1] J. T. Kelliher, J. T. Thornton, P. E. Russell, and K. J. Bachmann, Mater. Res. Soc. Symp. Proc. **317**, 597 (1994).

[2] N. Dietz, A. E. Miller, and K. J. Bachmann (unpublished).

[3] N. Dietz, A. E. Miller, J. T. Kelliher, D. Venables, and K. J. Bachmann, Proceedings of the Eighth International Conference on Molecular Beam Epitaxy, Osaka, Japan, 1994 (unpublished).

[4] Y. Horikoshi, Progr. Cryst. Growth Charact. **23**, 73 (1991).