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MULTIFUNCTIONAL OPTICAL *IN SITU* MONITORING OF SEMICONDUCTOR FILM GROWTH

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ABSTRACT

We have modified a normal-incidence optical reflectance spectroscopy system to allow rapid switching between the measurement of sample reflectance and sample emission. The resulting optical system is capable of "smart" pyrometry, in which sample emissivity is measured rather than assumed. The emissivity measurement makes use of the principle of detailed balance, which states that for specular, opaque samples, the sum of the emissivity and reflectance at each wavelength is equal to 1. We present data based on multilayer III-V semiconductor structures grown by molecular beam epitaxy, but the optical system would function equally well in any growth or deposition system with optical access to the substrate. The "smart" pyrometry temperatures we measure typically differs from conventional pyrometry by 5 to 10 °C, and occasionally as much as 20 °C, for multilayer structures of AlGaAs and GaAs. We present details of the optical components and arrangement that minimize the effect of sample wobble and allow the system operator regular visual access to the sample. Calibration techniques for the combined system are also discussed.

INTRODUCTION

In this paper we describe a single optical *in situ* monitoring instrument for both variable-wavelength optical reflectance spectroscopy (ORS) and pyrometric temperature measurements on semiconductor samples during epitaxial crystal growth. Combining the two techniques allows us to make "smart" pyrometry measurements in which the sample emissivity is measured rather than assumed. This change overcomes one of the largest limitations in the application of pyrometry to thin film deposition or etching. Conventional pyrometers measure the spectral radiance of blackbody radiation emitted from a target to measure its temperature. Conversion of the power to a temperature requires knowledge of the sample emissivity and the effective collection solid angle, that is, the actual solid angle corrected for any optical losses in the access path. Most pyrometers accept only a single number for the emissivity, which is assumed to be constant in time and over wavelength variations. This assumption introduces significant errors in growth and etching where thin film interference effects occur. The time variation of the emissivity has in fact been used successfully to monitor the thickness of epitaxial semiconductor layers with conventional pyrometers [1, 2]. The emissivity variations are particularly strong for growths that incorporate Bragg-reflector mirror stacks such as vertical cavity surface-emitting lasers and resonant cavity photodetectors [3, 4].

In situ monitoring using optical reflectance has been the topic of intensive research in the last several years [5–9], and pyrometry has been a standard industrial technique for measuring temperatures for some time. There are commercially available systems for making both measurements and at least one commercial system that combines them both. The previous published works and commercial systems generally do not address compensation for the limitations of the optical access to the system and the optical, mechanical, and electrical noise encountered in making measurements. Calibration issues are also rarely discussed. In this paper we therefore devote significant discussion to the unique aspects of our system with regard to optical-mechanical component selection, alignment, and calibration.

EXPERIMENT

The layout of the basic optical components in the multifunctional optical system is shown in Fig. 1. The basic elements are a broadband light source, a monochromator, focussing mirrors, bending mirrors, and a signal detector. A number of features of the layout make it uniquely suited for this work. Because of their bulk, the light source and monochromator are located on a shelf

near the growth system, and light is routed to the mirrors with a multimode optical fiber with a core diameter of 1 mm and a numerical aperture of 0.16. A 75 W xenon arc lamp is used for maximum wavelength flexibility; however, for many applications lower-cost quartz-tungsten-halogen lamps would be perfectly adequate. The mirrors and detector are mounted on a 20 cm x 20 cm optical breadboard that is bolted to a window flange on the growth system located at normal incidence to the sample. Mirrors are used for focussing primarily because they eliminate the need to refocus light as wavelength changes, especially into the ultraviolet and infrared where many lens materials show significant dispersion. A secondary benefit is that they allow the bending mirrors to be centered on the breadboard while still allowing the focusing optics to have relatively long focal lengths (10 cm for the light delivery and 15 cm for the light collection mirrors). The long focal lengths are important because the sample is located approximately 65 cm from the growth chamber window, and the magnifications of beam spot sizes and beam angles decrease as the focal lengths approach the sample distance. The 1 mm fiber core, for example, is magnified to about 7 mm on the sample, and refocused to about 1.5 mm on the detector. The image of a quarter of a 50 mm diameter wafer just fits on the 5 mm diameter silicon photodiode. An iris is mounted just in front of the detector to limit the collection area. The growth chamber window is continuously heated to prevent arsenic and phosphorus deposition.

For pyrometry data acquisition, the front bending mirror (closest to the window) is rotated out of the light beam, and an interference filter with 10 nm bandwidth is inserted in front of the detector. Two filters with different center wavelengths have been used in these experiments, one centered at 925 nm and one centered at 1000 nm. Because GaAs remains opaque at 925 nm to much lower temperatures than at 1000 nm, the 925 nm filter significantly extends the lowest accessible temperature (about 400 °C) with only a slight reduction in the emission signal intensity. The flat bending mirrors are mounted on high-precision rotating mounts that allow them to be flipped down to allow system operators visual access to the sample. The front bending mirror is motorized so that the control computer can switch between reflectance mode and pyrometry mode. A conventional optical pyrometer was also mounted on the rail supporting the breadboard to allow for comparison during these experiments.

A major challenge in any *in situ* measurement system is the fact that the sample position is usually both variable and not adjustable in a precise way. Although we have worked extensively with the growth system manufacturer to increase the stability of the sample rotation mechanism, the sample continues to wobble as it rotates because the rotation axis is not perfectly collinear with the sample normal. The direction of the rotation axis itself also drifts as the substrate manipulator is brought to growth temperature (typically 600 °C). The intrinsic wobble of the improved substrate manipulator is about $\pm 0.1^\circ$, but some sample holders can add another 0.1 to 0.5°. There are fundamental technological limitations on how well a system can allow the tolerances for load-locked sample transfer, ultra-high vacuum compatibility, high temperature operation, and sample rotation without some mechanical drifts and noise. As a consequence, the optical system must be designed to allow compensation for these effects. A small sample with minimal wobble is essential for the initial alignment. Alignment of the reflectance beam is undertaken with the monochromator set to zero wavelength (0-order diffraction) to get a bright white light that can be easily seen. The incoming beam fiber is positioned at a distance from the focussing mirror that puts the image of the fiber at the sample plane and centered on the sample. The substrate holder around the sample can generally be used as a screen for checking the spot focus. The collection optics are placed so that an image of the sample is formed on the detector. This image is most easily seen when the sample is hot enough that the holder emits substantial visible light.

Once the rough alignment is made, the primary adjustment is movement of the detector perpendicular to the beam to keep the sample image centered on the detector. If needed, the tilt of the front bending mirror is adjusted to keep as much of the return reflectance beam as possible in the window. The half-angle subtended by the window from the center of the sample is about 2.2° , so wobble angles of $\pm 0.5^\circ$ or more make it impossible to collect all of the reflected beam in the portion of the window unblocked by the incoming-beam optics. Even for smaller wobble angles we find that cyclic normalization [10] is helpful to correct for variations as the sample rotates. We deliver monochromatic light to the sample and collect the signal with a detector on the breadboard, unlike in our previous work in which white light was reflected off the sample and coupled into a fiber leading to the monochromator and detector. The coupling of a moving beam into a fiber and then to a monochromator produced very large wobble effects (30 % of the signal magnitude or more). Although the cyclic normalization can smooth out the variations, the day-to-day and sample-to-sample reproducibility of the signal intensity and hence the absolute reflectance are always in question.

The drawbacks of combining pyrometry and ORS are relatively minor. First, the pyrometer must be aligned to look at the sample at the same off-axis angle used by the reflectance system, reducing the available collection solid angle. Second, the collection optics must be set up to focus an image of the sample surface on the detector plane. The result is that the outgoing beam is large at the chamber window. Focussing the beam at the window exit point gives greater immunity to aperture effects in ORS especially on samples with large wobble. Third, the interference filter used in front of the detector is also sensitive to the angle of incidence, so the alignment of the beam to the detector must be more carefully monitored. Finally, because the signal strength is different in reflectance mode and pyrometry mode, a preamplifier with variable gain is needed for the photodiode, preferably an amplifier with a computer interface so that the switching between the different modes can be automated. In our system the reflectance signal at 925 nm is about 5 nA, and the pyrometry signal for a sample at 600 °C is about 0.1 nA. We use a lock-in amplifier and chopper to reduce noise in the reflectance signal, but the pyrometry signal cannot be modulated easily. It is therefore necessary to experiment with different grounding and shielding schemes to reduce noise from stray light and electromagnetic interference.

RESULTS

The errors arising in conventional pyrometry during thin film growth are shown in Fig. 2, a comparison of apparent temperature readings taken during the growth of an AlAs/GaAs Bragg reflector stack. The stack is designed for high reflectance at 650 nm at room temperature, and modeling predicts that the peak reflectance shifts to about 700 nm at growth temperature. We compare three types of measurements. The first set (solid circles) is derived from a conventional pyrometer with a bandpass of 60 nm centered on 940 nm. The second set (hollow circles) is the ORS system used as a conventional pyrometer with fixed emissivity. These readings diverge

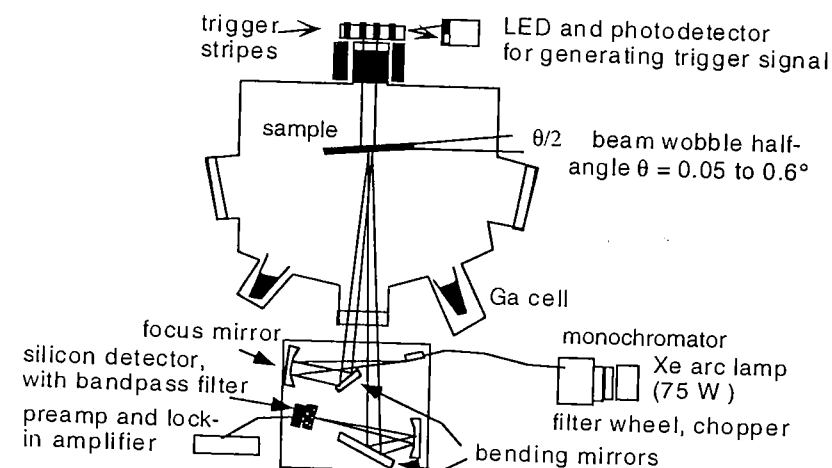


Fig. 1. Layout of the combined optical reflectance and pyrometry system, showing sample and rough schematic of the MBE growth system. The focussing and alignment optics, as well as the detector, fit on a optical breadboard that is bolted to the window flange. Conversion of the system from reflectance mode to pyrometry mode is accomplished by rotating the front bending mirror out of the beam path, inserting a filter in front of the detector, and changing the preamplifier gain.

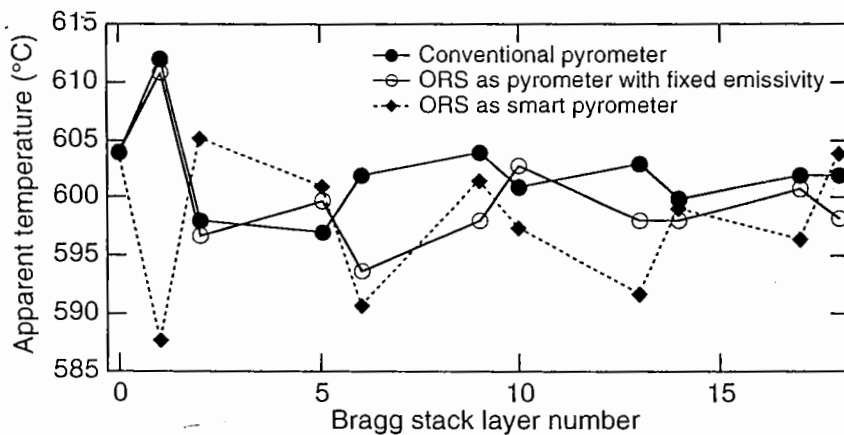


Fig. 2. Apparent temperature of a sample during a Bragg reflector stack growth of alternating layers of AlAs and GaAs. The reflector is designed for high reflectivity at 650 nm. The bandpass filter used for the pyrometry system is 1000 nm. Only the smart pyrometer correctly interprets the change in sample emission as its emissivity begins to deviate from its initial value.

from the conventional pyrometer because the ORS system uses a 10 nm band centered on 1000nm. Finally, the smart pyrometry data (diamonds with dashed lines) are derived from sample emission corrected for the measured changes in reflection over the same optical bandpass as the emission-collection filter. The emissivities used by each pyrometry configuration were taken from the reflectance of the bare substrate. The ORS pyrometer effective solid angles were set by matching the temperature calibration curves to the readings of the conventional pyrometer. As the data show, deviations as large as 20 °C can be observed over the course of the mirror stack growth. The smart pyrometer configuration shows that sample *cooling* is observed when the conventional pyrometer indicates sample *heating*. The cooling response is expected in our system because the sample heater is controlled by a thermocouple placed between the heater and the backside of the sample. When the front surface reflectance drops due to the antireflective properties of a thin, lower-index overlayer (AlAs), the sample emissivity increases and radiative heat losses increase. This increased emission is interpreted by a conventional pyrometer as an *increase* in sample temperature, when in fact the sample temperature has *decreased*. The emission has little impact on the thermal environment at the control thermocouple, so the sample heater does not compensate for this cooling unless it gets large.

The basic theory of pyrometric temperature measurements has been published in several places [11, 12]. The fundamental models are based on thermodynamic equilibrium theory applied to photon populations. The most familiar forms of the theory are expressed in the Planck distribution for blackbody radiation (usually integrated over the entire 4π solid angle) or the Stefan-Boltzmann law (integrated over all wavelengths). The theory can in fact be applied over a narrow solid angle and narrow wavelength range when the conditions for the principle of detailed balance [13] can be met. These conditions are that the sample be opaque at the wavelength in question and that the sample is specularly reflective (angle of reflectance equals angle of incidence) in order to prevent the mixing of nonequivalent momentum states for the photon populations. Under these conditions, the emissivity ϵ of the sample into a given solid angle at any wavelength is equal to $1-R$, where R is the reflectance measured into that same angle relative to the sample.

Although in principle the reflectance should be measured over the entire bandpass of the filter used for the pyrometry measurement, we find that measuring the reflectance at the center of the bandpass region provides sufficient accuracy for these measurements even for samples containing Bragg reflector stacks. This simplification is possible because the bandpass of the

filter is significantly narrower than the bandpass of a conventional optical pyrometer. Practical Bragg reflector structures are also designed for room temperature operation, and the changes in the layer optical constants in going from room temperature to growth temperature help to smooth out some of the sharper features. Figure 3 shows the reflectance measured over the entire bandpass for the 925 nm filter. With the exception of the wings of the filter where the signal is small, the reflectance is constant or with a slight trend that can be approximated by a line, the average value of which will be equal to the center value. To confirm this result we have modeled a variety of Bragg reflector stacks at growth temperature. The movement of the narrowest features through the pyrometer wavelength window does not cause the average emissivity to deviate more than 4 % from center wavelength emissivity. In critical applications, this error could be eliminated by sampling more wavelength points within the window. The single-wavelength simplification also means that if the filter's center wavelength is suitable for thickness measurements based on optical reflectance, then a separate reflectance measurement is not necessary for "smart" pyrometry corrections. A few seconds is all that is needed to determine the sample temperature and provide updated information to the temperature feedback loop, if needed.

A simple starting point for system calibration, used before acquiring the data in Fig. 2, is to alternate between a conventional pyrometer and the smart pyrometer for a bare GaAs substrate at a number of different temperatures. The conventional pyrometer is being used as a means of calibrating the effective solid angle of the smart pyrometer. We estimate the uncertainty in the temperature to be ± 2 °C, and this number should improve with further work. The reflectance and therefore the emissivity of the bare substrate can be calibrated by comparison with a sample of known reflectance. We have had good results with Si wafers coated with Al/MgF₂ layers similar to the coatings used on conventional metal mirrors. The reflectance of these Al/Si mirrors is measured in a calibrated spectrometer prior to loading into the system. The beam angle may be slightly different for the Al/silicon mirror and the bare GaAs substrate, so the sample alignment must be rechecked for each sample or after large temperature changes. When large adjustments are needed or when the sample wobble angle is greater than about $\pm 0.3^\circ$, it is no longer possible to be sure that the reflected beam is ever fully collected. In these cases the bare substrate itself provides the best reference signal using R values measured under more controlled conditions, for example, $R = 0.33$ for GaAs at 600 °C [5, 14]. The system also lends itself well to calibration with eutectics. Si wafers coated with about 100 nm of Al can be loaded in the system and monitored for absolute reflectance as they are heated. The roughening of the surface at the eutectic transition at 577 °C can be detected in the optical reflectance signal, and immediately switching the system to pyrometry mode allows an absolute temperature reference point.

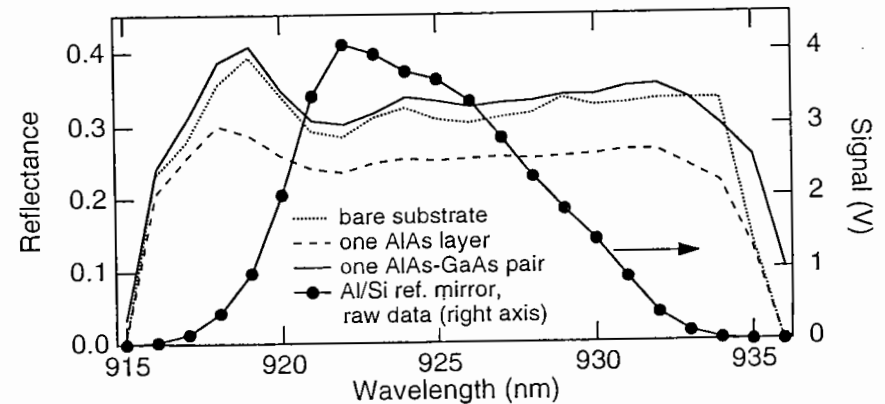


Fig. 3. Reflectance of sample during Bragg reflector stack growth scanned over the bandpass of a 925 nm filter, and the actual signal (right axis) from an Al/Si reference mirror used to normalize the raw data. The reflectance at the center of the filter bandpass provides a good approximation for the average reflectance in rapid smart pyrometry.

CONCLUSIONS

Combined optical reflectance and pyrometry offer a number of advantages over conventional pyrometry with little additional complications relative to a reflectance-only *in situ* optical system. The smart pyrometry possible with such a system produces more accurate results than conventional pyrometry. Alignment and calibration are still challenging, but we have found procedures that allow accurate measurements on samples if the wobble and axis direction drift are kept below $\pm 0.2^\circ$, a specification that is achievable in many semiconductor growth systems.

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IN SITU OBSERVATION OF SCALING BEHAVIOR DURING SOLUTION-PHASE GROWTH OF SURFACTANT MONOLAYERS

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ABSTRACT

"Self-assembled" monolayers of amphiphilic surfactant molecules form spontaneously on solid surfaces by exposure to dilute solutions of the adsorbate molecules. These monolayers are shown to form via a mechanism that includes nucleation, growth, coalescence, etc. of densely-packed submonolayer islands of the long-chain organic molecules. *In situ* atomic force microscopy experiments allow a quantitative analysis of island nucleation and growth rates as well as determination of the island size distribution as a function of coverage. In the growth regime, the nucleation and growth rates have a power law behavior consistent with a simple point island model of 2D cluster growth. The exponents are consistent with a critical nucleus of two molecules and the 2D diffusion coefficient corresponds to a "hopping time" of about 1 microsecond. In the aggregation regime, the island size distributions are shown to scale with a single evolving length scale in accordance with the dynamical scaling approximation.

INTRODUCTION

Self-assembled monolayers (SAMs) are formed by adsorption of amphiphilic organic molecules from dilute solution onto a solid substrate [1]. Generally, one end of the molecule has a strong and specific interaction with the particular substrate. This results in a robust monolayer where all molecules have the same orientation and conformation. Since the end of the molecule which does not attach to the surface can often be chemically tailored to have specific chemical properties, this sort of coating is promising for applications in controlling wetting, corrosion inhibition, prevention of bio-fouling, protein adsorption and catalysis, as well as more ambitious applications such as molecular electronics and biosensors.

Experiments in recent years have highlighted the similarities between these organic monolayers and more conventional epitaxial films, both their structure – which may be commensurate or incommensurate – and, more recently, their growth mechanism, which can be described qualitatively as a two-step process consisting of molecular adsorption from solution followed by organization into densely-packed 2D aggregates [2-10]. This formation process is clearly analogous to other types of thin film growth such as molecular beam epitaxy (MBE) [11] if we replace the solution-phase bulk transport by vapor-phase transport. Since Monte Carlo simulations and Smoluchowski-type rate equation approaches [12-14] have been quite successful in describing the 2D nucleation, aggregation, and coalescence process which occur during MBE growth, it is sensible to apply these theoretical tools to solution-phase monolayer growth as well. The real-time local information regarding the surface morphology obtained from our *in situ* atomic force microscopy (AFM) experiments allows a direct comparison between theory and experiment.