In situ temperature measurements for selective epitaxy of GaN nanowires

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We demonstrate with spatially resolved, in situ temperature measurements and ex situ reflectance measurements that differences in appearance for masked and unmasked surfaces on patterned growth substrates arise from wavelength-dependent emissivity variations and not from actual temperature differences. For this study, Si(111) substrates were coated with thin AlN buffer layers (about 40 nm thick) and then further coated with a SiNx mask layer (about 60 nm thick). “Blackbody” emission spectra were collected from homogeneous regions at growth temperatures near those that allow the selective epitaxy of catalyst-free GaN nanowires on the AlN by molecular beam epitaxy. The data were acquired with a commercial in situ diagnostic system that incorporates optical fiber collection to limit the sampling area to a circle about 5 mm in diameter on the substrate. The emittance spectra are estimated from room-temperature reflectance measurements. The implication for selectivity mechanisms and temperature measurements in molecular beam epitaxy in general are also discussed.

1 Introduction Selective epitaxy masks are widely used to control size and placement of epitaxial growth features [1-3]. The most common mask materials are silicon oxide and silicon nitride, both of which can be deposited as smooth thin films and readily patterned with photolithography, nanoimprint lithography, or electron beam lithography. We have recently shown that one successful scheme for selective epitaxy of GaN nanowires on Si substrates when grown with molecular beam epitaxy (MBE) consists of patterning a SiNx mask on AlN-coated Si(111) [4]. TiN and SiOx have also been shown to be effective masks for this materials growth process [5-8]. In MBE, radiative heat transfer processes play a significant role in determining substrate temperature, therefore the changes in surface emittance that accompany mask patterning could alter the local surface temperature and influence growth. At the high temperatures employed in GaN nanowire growth (around 820 °C), large mask features are easily distinguished by their color and brightness (see Fig. 1), creating the appearance of pattern-dependent surface temperature variations. Because temperature is a critical parameter in selective epitaxy, accurate surface temperature measurements are important in understanding how to control selectivity.

Figure 1 Visual appearance of patterned substrate at 815 °C. The AlN (two large squares and many small squares on a grid) appears brighter and more yellow than the surrounding SiNx mask. Color contrast in the photo has been artificially enhanced to approximate actual visual appearance.
In this paper, we show that the color differences observed between masked and open buffer areas do not correspond to actual changes in surface temperature. Simple thermal modeling also supports the conclusion that thermal transport in the underlying Si substrate is sufficiently high to prevent sustained temperature differences on the scale of the mask features on the basis of difference in surface emittance alone. Based on this demonstration of temperature homogeneity, we conclude that selective epitaxy for the mask features on the basis of difference in surface transport in the underlying Si substrate is sufficiently high to respond to actual changes in surface temperature. Simple estimates of the actual emittance changes on the temperature fitting algorithm, we exported the raw spectral data and fitted it with data analysis software. Because Si becomes partially transparent, even at high temperature, at the longer portion of the instrument wavelength range, the fits were performed in a more limited range of 930 nm to 1200 nm. Fits made to spectra without any emittance correction agreed with those returned by the commercial instrument to within one degree or better.

2 Experimental methods
2.1 Temperature measurement

Three temperature measurement methods were applied in this study. First, the growth system is equipped with a thermocouple located between the substrate heater element and the back side of the growth substrate. The substrate heater power is controlled with a feedback loop such that the temperature read by this thermocouple is equal to a programmable setpoint. As is widely known for MBE, the actual substrate temperature is typically tens or hundreds of degrees cooler than the thermocouple reading. As a more direct measurement of the substrate temperature, we also apply back-side pyrometry (BSP). With this method, we collect the blackbody emission spectra emitted from the back side of the wafer though a fused silica rod at the center of the substrate manipulator axis. The light passes through a vacuum window near the far end of the rod, where it is focused with a lens and then filtered with a 925 nm band pass filter, and finally measured with a silicon photodiode. This instrument operates on the same principle as commercial optical pyrometers, in which the temperature is determined from the total light intensity in a narrow wavelength band (10 nm in our case). Because the collection losses are difficult to calculate for this optical layout, we instead calibrate the BSP signal with blackbody temperature measurements on bare Si (see next paragraph) or with a commercial pyrometer pointed at a Si wafer target through a vacuum window facing the front side of the wafer.

The primary temperature measurement method applied is a commercial blackbody emission spectrum acquisition system. This system collects light emitted from the substrate through a vacuum window with a lens external to vacuum to focus the light onto an optical fiber, with an optical path along the substrate normal. The area of the substrate sampled by the fiber is a circle about 5 mm in diameter, and it can be located on the substrate by launching light from a red diode laser into the far end of the fiber. The patterned substrate was tested in this way to locate azimuthal rotation angles for which the collection area would be wholly on the mask region or over a bare buffer region. During spectral measurements, the fiber is coupled to a spectrometer calibrated to produce a flat intensity response for the lens/fiber/spectrometer path over the wavelengths $\lambda$, measured, about 930 nm to 1730 nm. According to manufacturer specifications, the transmission of the vacuum window is flat over this wavelength range as well. The spectra $I(\lambda)$ are fitted to the Planck distribution, parameterized as follows:

$$ I(\lambda) = C + \frac{\varepsilon(\lambda) \cdot A}{\lambda^5 \cdot (e^{\frac{hc}{\lambda kT}} - 1)} $$

where $C$ is a background count constant, $\varepsilon$ is the substrate emittance, $A$ is the tooling factor (a scaling constant to account for photon collection efficiency), $h$ is the Planck constant, $c$ is the speed of light, $k$ is the Boltzmann constant, and $T$ is the absolute substrate temperature. The limited wavelength range falls on the short wavelength limit of the spectrum, which peaks at about 2.7 $\mu$m. Although in principle, $\varepsilon$ is a function of wavelength, standard software assumes it is constant over the fitting range. This is a good assumption for a bare Si wafer, but the thin films used for buffer layers and masks add significant wavelength dependence. This effect measured over a narrow wavelength range allows measurement of film thickness during growth (emissivity-corrected pyrometry [9-11]). In order to estimate the effect of plausible emittance changes on the temperature fitting algorithm, we exported the raw spectral data and fitted it with data analysis software. Because Si becomes partially transparent, even at high temperature, at the longer portion of the instrument wavelength range, the fits were performed in a more limited range of 930 nm to 1200 nm. Fits made to spectra without any emittance correction agreed with those returned by the commercial instrument to within one degree or better.

2.2 Emittance measurement

Estimates of the actual emittance wavelength dependence began with measurement of the reflectance $R$ of large-area mask regions (SiN/AlN/Si) and buffer (AlN/Si) regions using a commercial spectrophotometer. The measured reflectance for the mask region is shown in Fig. 2. The spectrophotometer beam impinges on the sampled surface with an angle of incidence of $8^\circ$ relative to the normal. The $R(\lambda)$ data were modeled with a simple double-layer anti-reflection coating equation to extract suitable indices of refraction $n$ and film thicknesses $t$. The film parameters were varied over a range that produced moderately good agreement with the measured reflectance, specifically $n = 1.8$ to 1.9 and $t = 37$ nm to 38 nm for AlN, $n = 2.0$ to 2.2 and $t = 57$ nm to 65 nm for SiN, as shown by the dashed and solid lines in Fig. 2. The parameters agree well with literature values for index of refraction [12-14] and with SEM measurements of the film thicknesses. The Si substrate was modeled with $n = 3.42$, which works best for $\lambda > 500$ nm [15]. These parameters were then used to model the normal incidence $R(\lambda)$ corresponding to the growth chamber geometry, also shown over a more limited wavelength range in Fig. 2. The effect of high temperature on the indices of refraction was estimated as a 4% increase based on literature reports of
measurements on GaN films [16]. These models were converted to emittance models $\varepsilon(\lambda)$ using the simple thermodynamic relationship of $\varepsilon(\lambda) = 1 - R(\lambda)$ for an opaque sample. Examples of emittance models for each film are plotted against the right axis in Fig. 3.

3 Emittance correction Emission spectra from the mask (SiN$_x$) and buffer (AlN) regions of a hot substrate are shown in Fig. 3. Before emittance correction, the spectra for the mask and buffer regions look quite different, and fits of the spectra returned apparent temperatures of 859 ºC and 826 ºC, respectively, for the mask and buffer. The spectra were then corrected by dividing each point by the emittance model values determined in the previous section. The resulting emission spectra become almost identical, and fits return temperatures of 824 ºC and 822 ºC, respectively, for the mask and buffer. Most of the shift occurs in the mask temperature measurement. The temperature returned by the fit is determined mostly by the slope of the curve, rather than the absolute value of the emission intensity. Although the buffer emission curves shift upward after emissivity correction, this shift is mostly a constant factor correction and does not affect the temperature returned by the fit.

This procedure was repeated for emission spectra taken over a range of substrate thermocouple temperatures relevant to GaN nanowire growth. As a way of estimating the uncertainty in the emittance-corrected temperature values, several different $\varepsilon(\lambda)$ models were generated from the range of indices and thicknesses above, in some cases applying the index temperature correction and in some cases not. The resulting variations in emittance are about 1.5% of the average values. As shown in Fig. 4, the mask and buffer layer temperature appear to be quite different before emittance correction, but become equal within experimental uncertainty after correction. The corrected temperatures also agree quite well with blackbody measurements on bare Si substrates, for which the assumption of a flat emissivity spectrum is a good one. After emittance correction, the tooling factor $[A$ in Eq. (1)] also increased by about 50% for both mask and buffer layer fits.

4 Discussion The apparent temperature differences returned by the uncorrected emission spectra fits are significant relative to the temperature range over which selective epitaxy can be achieved for GaN nanowires. The growth window varies with Ga and N flux, but generally spans only about 30 ºC between selective growth and complete re-evaporation of Ga (no growth). We have shown here, however, that these temperature differences are not real, but rather an artifact of emittance wavelength variations. These variations can be modeled with simple thin film reflectance equations that ignore wavelength dependence in the indices of refraction of the films. Because the temperature measurement takes place over a wavelength range well below the band gap of the film materials, this assumption is adequate for the task. Because we can conclude there are no spatial variations in temperature, the mechanism that drives selectivity must involve surface-dependent activation energy variations in processes such as Ga desorption or diffusion.
regions (SiNx) and open buffer regions (AlN) both before (hollow symbols) and after correction (solid symbols) for surface emittance. The blackbody temperature for bare Si is also shown without correction.

As a further check on the experimental result, we have performed a simple worst-case estimate of the temperature difference that could be sustained due to radiative heat loss from a small mask opening with area 1 µm². The Stefan-Boltzmann equation indicates that the radiative heat loss \( q \) at 860 °C for such a surface with \( \varepsilon=1 \) would be about 90 nW. If the same amount of heat were flowing into the hemisphere of radius \( r \) under that open surface area, the maximum temperature difference from the edge to the center, \( \Delta T \), is \( q/r/\kappa = 10^{-14} \) K. In this estimate, we use \( \kappa = 30 \) W m⁻¹ K⁻¹, taken from literature values for Si at high temperature [17]. A larger thermal gradient could be sustained for a larger opening, but even for an area of 1 cm², the thermal gradient is negligible. (The hemispherical boundary model would not be a good approximation for such larger openings.)

The reflectance measurements also indicate that in the visible range, the buffer layer has a higher overall emittance than the mask layer, and has an emittance that favors the shorter end of the visible spectrum (not shown), while the mask emits more strongly in the red. The color differences in Fig. 1 are therefore explained by the thin film interference patterns modeled in Fig. 2.

These results also show that even modest alterations of the wavelength dependence for the collected emission spectra will introduce significant errors in blackbody temperature modeling. Window deposits that occur in MBE growth are therefore another potential source of error in applying these methods. Even when these deposits appear spectrally neutral (gray), we have observed that the variations in infrared transmission can easily induce artificial shifts of > 50 °C.

5 Conclusions Thin-film changes in surface emittance may lead to large systematic errors in surface temperature determination from blackbody emission spectra. The true surface temperatures can be recovered with emittance modeling based on reflectance measurements. Our results show that common mask schemes for selective epitaxy by MBE do not produce differences in surface temperature between mask regions and openings.

References