Emission Infrared Spectroscopy for In Situ Analysis of the OMVPE Growth Surface

D. MAZZARESE, K. A. JONES* and W. C. CONNER
Department of Chemical Engineering, University of Massachusetts, Amherst, MA
*Electronics Technology and Devices Laboratory, Fort Monmouth, NJ

Fourier transform infrared (FTIR) spectroscopy has proven to be an effective tool for the analysis of OMVPE growth. Both transmission and attenuated total reflection (ATR) provide information including identification and the relative concentrations of both reactants and products. Until recently we have only been able to apply transmission to the gas phase and ATR to in situ surface analysis. OMVPE is a heterogeneous process and ATR using a GaAs element is limited to temperatures where the sample is transparent, i.e. <400°C. Surface reactions are important to the overall process. We have recently developed a technique which effectively monitors the surface species in situ. All materials emit infrared radiation proportional to T^4. Under OMVPE growth conditions (400-700°C) this emission is considerable, particularly from the surface of the emitting sample. Emission spectra correspond directly to that of absorption spectra and can easily be collected with an FTIR spectrometer. The spectra yield the same information as transmission FTIR primarily for surface species. We have used this system to monitor the adsorption and reaction of TMGa and ammonia. We have identified adsorbed ammonia and TMGa on the surface and have been able to see how these molecules change as they decompose on the surface.

Key words: Surface kinetics, gallium nitride, trimethylgallium adsorption

INTRODUCTION

Organometallic vapor phase epitaxy (OMVPE) involves a number of complex chemical reactions. It has been shown that precursors such as tertiarybutylarsine and tertiarybutylphosphine partially decompose in the gas phase, 1,2 while others including AsH₃, PH₃, and NH₃ decompose on the surface. Either way, final heterogeneous steps are required for the incorporation of group III and group V atoms into the growing film. Models of OMVPE growth contain surface reactions which lead to final product. 3 Experimental verification of surface species would be useful in determining which models best represent the important surface chemistry.

Reaction surfaces have been monitored during growth using reflectance difference spectroscopy, 4 optical pyrometry, 5 and laser reflectometry. 6 These studies yield information such as growth rate and surface coverage. Unfortunately, none of these techniques can determine precisely what surface species are present.

Infrared attenuated total reflectance spectroscopy (ATR) can be used to observe the vibrational bands of molecules adsorbed on GaAs single crystals by using the GaAs crystal as an infrared wave guide. 7,8 The problem with ATR is that it is limited to about 400°C, 9 with the best spectra being collected below 100°C. 10 In either case these temperatures are below those used in most III/V OMVPE growth reactors. The reason ATR has this temperature limitation is that it requires the infrared light to be transmitted through the GaAs sample. As temperature increases thermal electron absorption becomes significant making it difficult to transmit the infrared light through the crystal. 11 One can show that the reflectivity increases as the absorption coefficient increases. 12 Thus as temperature increases the GaAs crystal changes from a low temperature infrared transmitter to a high temperature infrared mirror.

All materials emit infrared radiation. For a black body this emission is proportional to temperature to the fourth power. For gray bodies the emission closely resembles black body emission at frequencies that correspond to vibrational transitions of the solid and any adsorbed species. For other frequencies emission is much less. Since atomic layer epitaxy (ALE) works one can state that the surface of the GaAs crystal is covered with reactant after each exposure. 13,14 The combination of GaAs acting as a mirror and the high coverage of surface species at reaction temperature make infrared emission spectroscopy an effective way to observe surface species at reaction temperature.

Infrared emission spectroscopy has been used in catalysis to study surface reactions. 15,16 It has been shown in these studies that the vibrational bands found by emission spectroscopy are the same as those measured using transmission spectroscopy. 17 Several good sources are available with vibrational spectra of adsorbed and complexed molecules. 18-20 This means that once an emission spectrum is properly collected identification of the bands should be relatively straightforward. The resulting spectra should provide insight into species present on the surface at reaction temperature. Additional information about surface emission spectroscopy can be found in the literature. 21-23

(Received April 29, 1991; revised July 26, 1991)
EXPERIMENTAL

For the experiments conducted a resistance heated GaAs sample was placed in our gas flow cell. This atypical OMVPE system allowed us to collect emission spectra and monitor the surface in situ. One should note that material grown was far from device quality. The gas cell/reactor, shown in Fig. 1, was designed and built by Harrick Scientific. It can be evacuated to 10⁻⁶ Torr, exposed to reactive gases, and heated to 800 °C. The multidirectional infrared emission goes through the infrared transparent ZnSe window and is focused by the parabolic mirror. The emitted light is then sent into the Nicolet 7199 interferometer. Figure 2 shows where the cell is placed in the optical path of a Fourier Transform Infrared Spectrometer (FTIR). The only major change made to our spectrometer was to remove the infrared source from the beam path and replace it with our gas cell. Thus we use our GaAs sample as the infrared source. Once the cell was fixed with the emitted radiation aligned to the optical path, the system was ready for data collection.

The system is currently set up to examine trimethylgallium (TMGa), and NH₃. Solid semiconductor samples are typically heated in flowing hydrogen to remove any oxide, then exposed to reactant gases at low pressure (0–10 torr). In the initial experiment we exposed the clean GaAs surface to either NH₃ or TMGa. The samples were then alternately exposed to single gases (NH₃, TMGa, H₂).

The (100) GaAs crystals were prepared as follows: degreased with trichloroethylene, etched with a 3/1/1 solution of H₂SO₄/H₂O₂/H₂O, rinsed with deionized water, and dried in nitrogen. After this cleaning a sample would be placed in the reactor and heated to 600 °C in flowing hydrogen (10 sccm 30 Torr). We determined the surface to be oxide free by monitoring surface emission bands of the GaAs oxide at 1100 cm⁻¹. When we could no longer see any change in this band we considered the surface oxide to be removed. Hydrogen was evacuated from the gas cell and a background spectrum was collected at the experimental temperature. Auger Electron Spectroscopy (AES) indicated that the surface was Gallium rich after this preparation technique. After cleaning the sample would be exposed to ~10 Torr of a reacting gas. The system would then be pumped down to 0.5 Torr or less and a spectrum of the surface would be collected. This spectrum would be ratioed to the background to separate the emission of the cleaned bulk crystal. The result is an emission spectrum of the reagent adsorbed on the GaAs crystal.

It should be noted that neither baseline correction nor data smoothing was used on the spectra...