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Unexpected Bismuth Concentration Profiles in MOVPE GaAs$_{1-x}$Bi$_x$ Films Revealed by HAADF STEM Imaging

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Recent interest in the growth of GaAs$_{1-x}$Bi$_x$ semiconductor alloys with controlled Bi concentration has been stimulated by the sensitivity of the bandgap energy and valence band structure to Bi concentration, x. These sensitivities offer the possibility to engineer both the band gap and band offsets at junctions to improve the performance of devices. Realization of this potential, however, requires development of thin film growth techniques that coax Bi atoms into a GaAs lattice in which they are insoluble. Electron microscopy studies are critical to the materials characterization that is needed to understand and then control how Bi atoms, with large atomic radius and electronegativity differences relative to the As atoms they must replace, are distributed within the metastable GaAs$_{1-x}$Bi$_x$ materials and, ultimately, device structures grown.

X-ray diffraction analyses of multilayer structures commonly are used to study the growth of new semiconductor materials. Typically thickness, growth rate, and composition of a material under exploration are deduced from the superlattice and crystal lattice periodicities that are revealed in high-resolution x-ray diffraction patterns. These analyses usually involve fitting a concentration profile of assumed shape, but unknown magnitude, to infer the compositions of the layers in the structure. The assumed shape often mirrors the variations in the precursor (atomic fluxes) used to grow the structure by MOVPE (MBE) techniques. Following this practice, good fits to the x-ray diffraction pattern data from the MOVPE GaAs$_{1-x}$Bi$_x$/GaAs multilayer quantum well structures investigated in this study were obtained for square-wave shaped concentration profiles. These fits provided critical information regarding the growth rate of the multi layer structure and its average Bi concentration. The study reported here used the HAADF imaging technique in an aberration corrected STEM to explore more directly how the incorporated Bi was distributed in the growth direction.

GaAs$_{1-x}$Bi$_x$/GaAs quantum well superlattices were grown on nominally singular, [001]-oriented GaAs substrates in a low-pressure MOVPE horizontal reactor using the “pulsed” Bi precursor method described in [1]. In this method, the Bi precursor chemical is pulsed asynchronously with the Ga precursor during growth of the GaAs$_{1-x}$Bi$_x$ layers. Continuous flows of the Ga and As precursors are introduced during GaAs barrier layer growth. TEM samples were prepared using mechanical wedge polishing to a roughness of <1 μm, followed by Ar ion milling. HAADF images were acquired in a FEI Titan STEM with a CEOS probe aberration corrector operating at 200 kV. Images were collected with a 24.5 mrad probe semiangle, HAADF detector range of 54-270 mrad and STEM resolution of ~0.8 Å.

A HAADF STEM image extending from the GaAs buffer layer approximately one GaAs$_{1-x}$Bi$_x$/GaAs bilayer period into a structure grown at 420°C is presented in Fig. 1(a). Fig 1(b) shows the intensity profile along a 10 nm wide line cut perpendicular to the interface. Both suggest immediately that a much more complicated Bi concentration profile exits in the sample than the square-wave function anticipated. Specifically, seven oscillations in the image intensity are detected in the first 15 nm of growth, followed by a broad, higher intensity peak with tails that trend over the next 15 nm of growth toward the intensity generated in the GaAs substrate. This intensity pattern was repeated in each of the eight periods of the superlattice (not shown in Fig 1). The seven peaks almost certainly correlate with the seven individual pulses of Bi precursor used to grow the GaAs$_{1-x}$Bi$_x$ well layer. They thus also indicate where in the profile the growth of the well was intended. The Bi precursor flux is shut off after the seven pulses in order to grow a GaAs barrier layer. The HAADF image indicates, however, that Bi not only continues to be incorporated into the growing structure during “barrier layer” growth, but in fact does so at an accelerated rate. The result presents a twist: the superlattice structure that results is comprised of Bi-rich well layers and Bi-deficient barrier layers, but the bulk of each grows when the other is intended to.3

The Bi concentration values indicated in Figure 1(b) were deduced using the formalism proposed in [2] weighted linearly with HAADF image intensity by accounting for the total mass of Bi in the superstructure that was revealed in the x-ray diffraction analysis.

The combined x-ray and HAADF STEM results demonstrate the importance of investigating the concentration profiles attained when new chemistries are used to grow new alloy thin films before relying solely on x-ray measurements for composition determination. They also suggest that the mechanisms for Bi incorporation in GaAs is a complex chemical and diffusional process that must be understood before film growth can be engineered.

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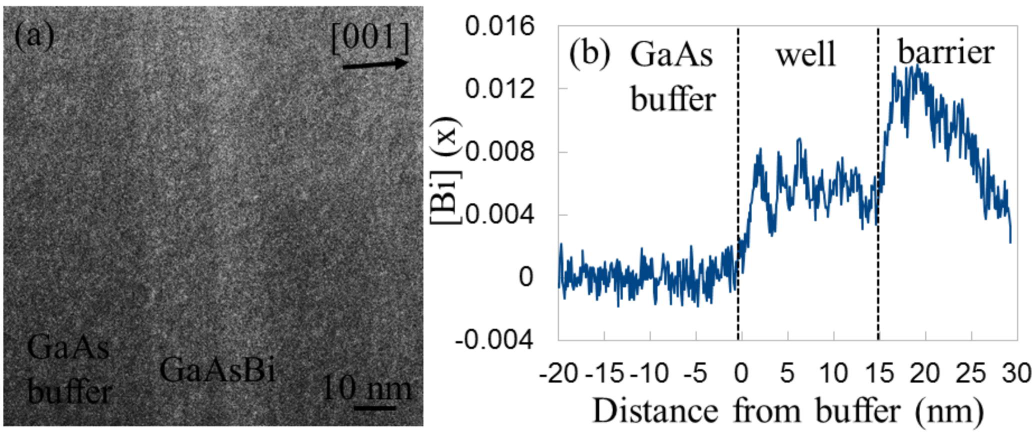

Figure 1. (a) HAADF STEM of GaAsBi/GaAs bilayer grown 420ºC and (b) corresponding Bi concentration profile deduced from a line scan of the image intensity and the x-ray diffraction-based determination of total Bi content.