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Ordering-induced band structure effects in $GaInP_2$ studied by ballistic electron emission microscopy

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We have analyzed the second voltage derivative (SD) of the ballistic electron emission microscopy (BEEM) spectra of $GaInP_2$. We associate two peaks observed in the SD-BEEM spectra of disordered $GaInP_2$ on n^+ GaAs substrate with the Γ and L conduction minima, $\Delta(\Gamma-L) \sim 0.35$ eV. An additional third peak appearing in the SD-BEEM spectrum of ordered $GaInP_2$ ($\eta \sim 0.5$) is associated with the L-band splitting due to the ordering-induced ''folding'' of one of the four L valleys onto the $\bar{\Gamma}$ point. According to our results, this splitting is $\sim$ 0.13 eV. © *1999 American Institute of Physics.* [S0003-6951(99)02434-1]

In the past decade, spontaneous CuPt ordering of many III–V alloys has been widely observed in vapor phase growth on (001) substrates. In $GaInP_2$, extensive theoretical[1,2] and experimental[3] work has been carried out to study the effect of the ordering-induced reduction of the crystal symmetry on the structural, optical, and transport properties of the ordered material. The most pronounced effects are the increase of the carrier mobility,[4] splitting at the valence band, lowering of the fundamental band gap relative to the random alloy, and the folding of the L conduction band on the $\bar{\Gamma}$ point.[1] These variations have a complex dependence on the growth conditions such as growth rate, growth temperature, and III–V ratio.[5] Dependence of the material parameters on the degree of ordering is also exploited in the device design of, for example, bistable polarization switches,[6] polarization convertors,[7] orientational superlattices,[8] visible light-emitting diodes,[9] and semiconductor lasers.[10,11]

Perfectly ordered material has not been observed. In the most ordered $GaInP_2$ structures, the highest ordering parameter $\eta \sim 0.6$,[12] and the degree of ordering is nonuniform on the local scale. Ballistic electron emission microscopy (BEEM), a three-terminal modification of scanning tunneling microscopy, has recently been shown to be a powerful tool for nanometer-scale characterization of the spatial and electronic properties of semiconductor structures. Since the pioneering work of Kaiser and Bell,[13] the capability of BEEM to probe the electronic properties of semiconductors on the local scale has been demonstrated in several systems, including Schottky contacts[14,15] and buried heterojunctions.[16–18]

In this letter, we report a quantitative study of the second voltage derivative (SD) BEEM spectra of Au/GaAs/$GaInP_2$ heterostructure for probing multivalley hot electron transport. The SD-BEEM current is approximately the heterostructure transmission coefficient,[19] and, therefore, allows an explicit energetic partitioning of the transport channels. The obtained SD-BEEM spectra of ordered and disordered GaInP on n^+ GaAs substrates show a clear distinction that we associate with the L-band splitting due to the ordering-induced ''folding'' of one of the four L valleys onto the $\bar{\Gamma}$ point.

The undoped GaAs/$GaInP_2$ structures on n^+- and p^+-GaAs substrates were grown by metalorganic chemical vapor deposition (MOCVD), at $T_g = 650\,^\circ$C. The structures consist of a 500 Å undoped GaAs buffer layer, a 1 μm $GaInP_2$, and a 50 Å GaAs cap layer. A detailed analysis is presented here for the $GaInP_2$ samples grown on a (511) GaAs substrate and on a (001) GaAs substrate misoriented 6° toward $[111]_B$. From the low-temperature photoluminescence, the band gap energy (after correction on the exciton binding energy) is $\sim$2.00 eV for $GaInP_2$ grown on a (511) GaAs substrate and $\sim$1.88 eV for $GaInP_2$ grown on a $6^\circ[111]_B$-(001) GaAs substrate. Therefore, we conclude that the $GaInP_2$ layer grown on a (511) GaAs substrate is highly disordered (hereafter, disordered $GaInP_2$) and the $GaInP_2$ grown on a (001) GaAs substrate misoriented 6° toward $[111]_B$ is highly ordered, $\eta \sim 0.5$ (hereafter, ordered $GaInP_2$).[2] For comparison, we also present results for a 1 μm undoped GaAs layer grown on n^+ and p^+ GaAs, the reference GaAs samples.

To fabricate diodes for BEEM, Au layers (1 mm in diameter and 60 Å thick) were deposited by thermal evaporation on the GaAs cap layer to form the metal base and indium ohmic contacts were soldered to the back of the GaAs substrate to form the collector contact. The details of the fabrication procedure have been published elsewhere.[17] The measurements were performed in a Surface/Interface AIVTB-4 BEEM scanning tunneling microscope (STM) using a Au tip. Room temperature experiments were performed in air, while for the lower temperature experiments, the STM head with a sample was immersed in cold He exchange gas in a nitrogen-cooled dewar. The tip-to-base voltage (V_t) was

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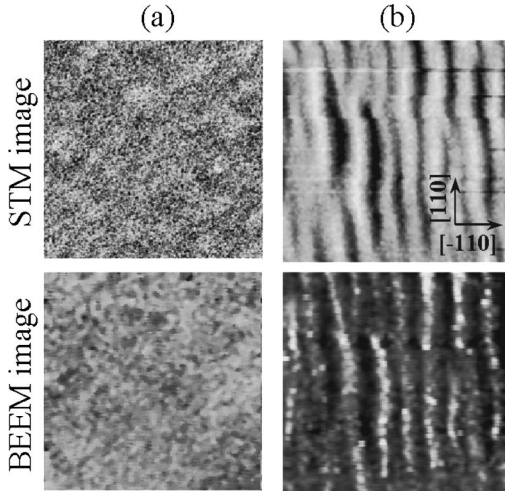

FIG. 1. Room-temperature 1 μm×1 μm STM image (top) and BEEM image (bottom) of GaAs/GaInP$_2$ layer grown by MOCVD on (a) (511) n-GaAs substrate, (b) on (100)n-GaAs substrate misoriented by 6° to $[111]_B$. A tip bias is −1.7 V and a tunnel current is 4 nA.

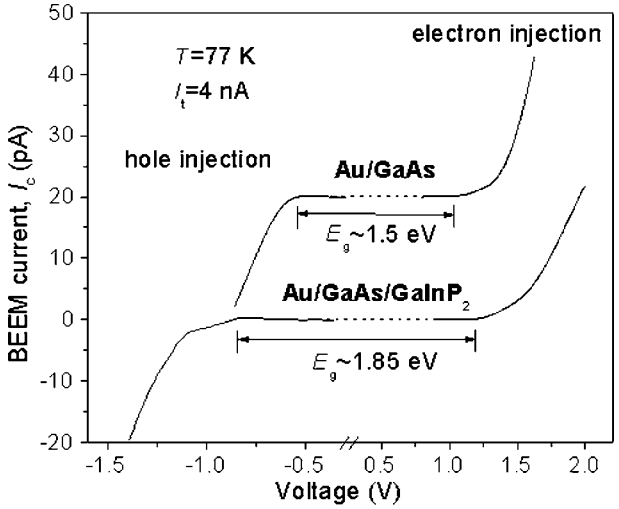

FIG. 2. BEEM spectra (77 K) of Au/GaAs/GaInP$_2$ and reference Au/GaAs samples grown on n-type (right side) and p-type (left side) GaAs substrates. For clarity, the spectra are shifted along the vertical axis.

varied between 0.7 and 2 V to acquire the collector current (I_c) while keeping a constant tunneling current (I_t) of 4 nA. A typical BEEM current value is ~30 pA at 0.5 V above the threshold, and a typical noise level is about 0.5 pA. The spectra were typically averaged for several thousand scans to improve the signal-to-noise ratio.

Figure 1 shows room-temperature 1 μm×1 μm STM images of the disordered (a) and ordered (b) GaInP$_2$ layer grown on n^+-GaAs substrates. One can see that the surface of ordered material forms [110]-oriented steps. For ordered GaInP$_2$ grown on misoriented substrates, the [110] steps are usually observed to form only single CuPt variant.[20,21] For disordered GaInP$_2$, the surface is found to be much flatter than that of ordered GaInP$_2$. The complementary BEEM images are also shown in Fig. 1. The observed contrast of the BEEM image for the ordered GaInP$_2$ sample is in direct correlation with the surface morphology, indicating high sensitivity and high spatial resolution of the BEEM technique.

Representative BEEM current dependencies on the applied tip-to-base voltage are presented in Fig. 2 for 1 μm undoped GaAs and GaAs/GaInP$_2$ layers grown on n^+- and p^+-GaAs substrates. The sum of the Schottky barrier heights for the electron and hole injection equals approximately the band gap energy of the semiconductor, namely ~1.5 eV for GaAs and ~1.85 eV for GaInP$_2$. We found that the band gap discontinuity is accommodated mostly by the valence band. GaAs/GaInP conduction band offset is ~0.1 eV and GaAs/GaInP valence band offset is ~0.3 eV, in general agreement with previously reported experiments.[22,23]

The SD spectra were obtained from the experimental BEEM spectra by numerical differentiation with a 10 meV window, and are shown in Fig. 3. We associate two clearly pronounced features in the 77 K SD-BEEM spectra of disordered GaInP$_2$ with the Γ and L conduction minima contribution in GaInP$_2$. Theoretical fit to the SD-BEEM spectrum for the disordered GaInP$_2$ sample, using the m-s interface-induced scattering (MSIS) model,[24,25] are shown in Fig. 3 by the dashed line. The MSIS model fit describes the experimental BEEM spectrum reasonably well, giving ~90% probability of the electron scattering at the m-s interface, similar to our previous results for GaAs/AlGaAs structures.[25] The absence of a contribution from the X conduction minimum is due to strong X-electron attenuation in the GaAs cap layer.[26]

The SD-BEEM spectrum of the ordered GaInP$_2$ sample presented in Fig. 3 shows a very important difference from that of the disordered GaInP$_2$. Namely, we observe two high-energy peaks instead of one peak in disordered GaInP. It is very unlikely that we start to observe the X valley contribution, because both samples (ordered and disordered) contain the GaAs cap layer and, therefore, the X-electrons attenuation is expected to be the same. We assign both high-energy peaks to be associated with the L valley contribution. In CuPt-type ordered GaInP$_2$, one of the four L valleys folds onto the $\bar{\Gamma}$ point (hereafter L_Γ), and the other three are folded onto the $\bar{D}$ point (hereafter L_D). A strong repulsion between the Γ valley and the folded L_Γ valley results in the band gap reduction and in the increase of the $\Gamma - L_\Gamma$ separation, while the energetic position of the L_D remains almost

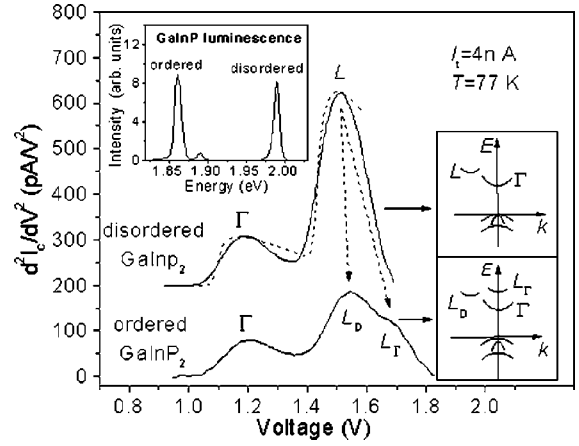

FIG. 3. SD-BEEM spectra for two GaAs/GaInP$_2$ (ordered and disordered) samples with 50 Å GaAs cap layers, taken at $T=77$ K. For clarity, the spectra are shifted along the vertical axis. The MSIS model calculations are also presented (dashed line). The top inset shows the photoluminescence spectra for both ordered and disordered GaInP samples, whereas two bottom insets show the schematic of the GaInP band structure.

the same. Therefore, we conclude that the two observed high-energy peaks for the ordered sample are the contribution of the L valleys that are split due to ordering.

As a consequence of the L valley splitting in the ordered sample, the absolute height of the L peaks in the SD-BEEM spectrum decreases compared to the L valley contribution in the disordered sample, but the overall area under the two peaks is about the same as the area under the single L peak for disordered GaInP. The experimentally obtained ratio of ~ 2.5 between the integrated contribution of L_D and L_Γ is very close to the expected value of 3 (considering only the number of folded valleys without taking into account the effective mass modifications).

The folded zone-edge bands were observed experimentally in electro-reflectance[26] and Raman spectroscopy[27] measurements. In the recently reported electro-absorption experiments on ordered $GaInP_2$ ($\eta \approx 0.45$),[28] an additional feature was observed at ~ 0.48 eV above the fundamental band gap transition, and this feature was attributed to the back folded L conduction band. As the ordering decreases, this peak shifts to lower energies, with an asymptotic value of ~ 0.33 eV above the fundamental band gap transition for a totally disordered sample. In Refs. 26–28, due to the selection rules, only the contribution from the L valley folded onto the Γ point was observed. In contrast, we observe the contribution from all L valleys and, as a consequence, can measure directly the $\Gamma - L$ separation in disordered $GaInP_2$ as well as the ordering-induced L valley splitting in ordered $GaInP_2$. According to our results, $\Delta(\Gamma - L) \cong 0.35$ eV for a disordered sample, $\Delta(\Gamma - L_\Gamma) \cong 0.47$ eV and $\Delta(L_\Gamma - L_D) \cong 0.13$ eV for an ordered sample.

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