Atomic ordering of GaInP studied by Kelvin probe force microscopy

Y. Leng and C. C. Williams[a)]
Department of Physics, University of Utah, Salt Lake City, Utah 84112

L. C. Su and G. B. Stringfellow
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

(Received 3 October 1994; accepted for publication 22 December 1994)

The atomic ordering of GaInP has been established and studied by a variety of methods, including transmission electron microscopy, cathodoluminescence, and photoluminescence. In this work, a Kelvin probe force microscope (KPFM) has been employed to image several GaInP samples previously characterized by these established techniques. The results of our study clearly show that the KPFM is capable of distinguishing between ordered and disordered regions in GaInP, and that the KPFM contrast strongly depends on the amplitude of the applied ac bias voltage of the KPFM. The measurements indicate that ordering in GaInP modifies the density and/or lifetime of the surface states. © *1995 American Institute of Physics.*

Under certain growth conditions, GaInP lattice matched to GaAs spontaneously orders on the group III sublattice with gallium and indium atoms occupying alternating {111} planes.[1] The ordering is identified by the appearance of superspots in transmission electron diffraction (TED) patterns. The formation of the ordered structure reduces the energy band gap of GaInP, as observed by cathodoluminescence (CL)[2] and photoluminescence (PL).[3] Ordering also influences the transport properties of GaInP, as shown in the current-voltage characteristics of Al-GaInP Schottky diodes.[4] Surface kinetics is believed to play an essential role in the formation of the ordered structure. Recently, atomic force microscopy (AFM) has been used to study the correlation between the surface morphology and the ordering.[5,6] It was shown that the formation of facets strongly influences the growth of ordered GaInP. In this work, a Kelvin probe force microscope (KPFM) is used to study the relation between ordering and the electronic properties of the surface of GaInP.

The KPFM used in this work is a modified non-contact mode AFM, capable of simultaneously measuring surface topography, surface potential, and capacitance.[7,8] Figure 1 contains the block diagram of our KPFM. A detailed description has been published elsewhere.[9,10] Briefly, an electrochemically etched tungsten tip is attached to a reflective glass cantilever, with a spring constant typically of about 10 N/m, and a resonant frequency about 5 kHz. A differential interferometric detection system is used to detect the motion of the cantilever. While a feed-back loop is used to maintain a constant force gradient (for topographic imaging in non-contact mode), an extra voltage $A\cos(\omega t)$ is applied to the tip with sample being grounded. The electrostatic force between the tip and sample, F, is given by:

$$F=\frac{1}{2}\frac{\partial c}{\partial z}(\delta\phi+A\cos\omega t)^2, \tag{1}$$

where c is the capacitance between the tip and sample, z is the gap distance between the tip and sample, A is the amplitude of the applied ac voltage, and $\delta\phi$ is the electrostatic potential difference between the tip and sample surface. The amplitude of the electrostatic force at frequency ω (F_ω) is proportional to $\delta\phi$. The cantilever movement at frequency ω is detected through a lock-in amplifier, and a second feedback loop is used to add a dc voltage to the tip (bucking voltage) to maintain F_ω at zero. This bucking voltage directly represents the local sample surface potential.

A force ($F_{2\omega}$) is also detected at twice the ac bias frequency. This force is related to the capacitance between the tip and sample. If the gap distance is maintained constant, any change in the $F_{2\omega}$ is due to the local capacitance variation.

All of the GaInP samples studied in this work were grown by organometallic vapor phase epitaxy (OMVPE) on semi-insulating GaAs substrates. The first sample under study (SU-10) is a GaInP order/disorder bilayer heterostructure, which was grown on a (001) GaAs substrate, with a 3° misorientation toward [$\bar{1}$10] direction. The first layer was grown at 740 °C and the second at 620 °C. Growth was interrupted for 5 minutes between layers by stopping the group III flow while keeping the phosphine partial pressure unchanged. Due to the temperature influence on ordering, the bottom layer, grown at 740 °C, produces a disordered structure, with a thickness of 0.5 μm, while the top layer, grown at 620 °C, is highly ordered, with a thickness of 0.4 μm. A schematic diagram of this order/disorder heterostructure is shown in Fig. 2(a). The sample has been well characterized

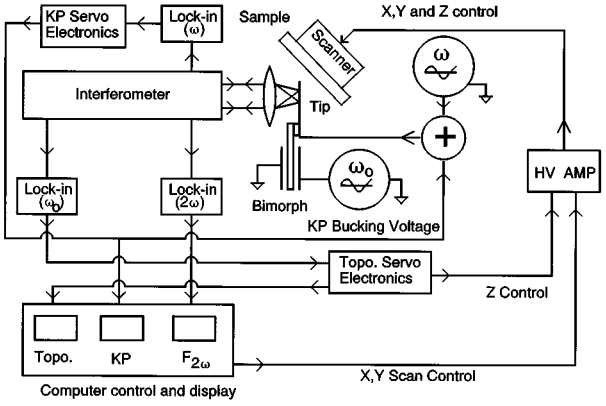

FIG. 1. Block diagram of KPFM.

[a)]Corresponding author (electronic mail: clayton@mail.physics.utah.edu)

 0003-6951/95/66(10)/1264/3/$6.00

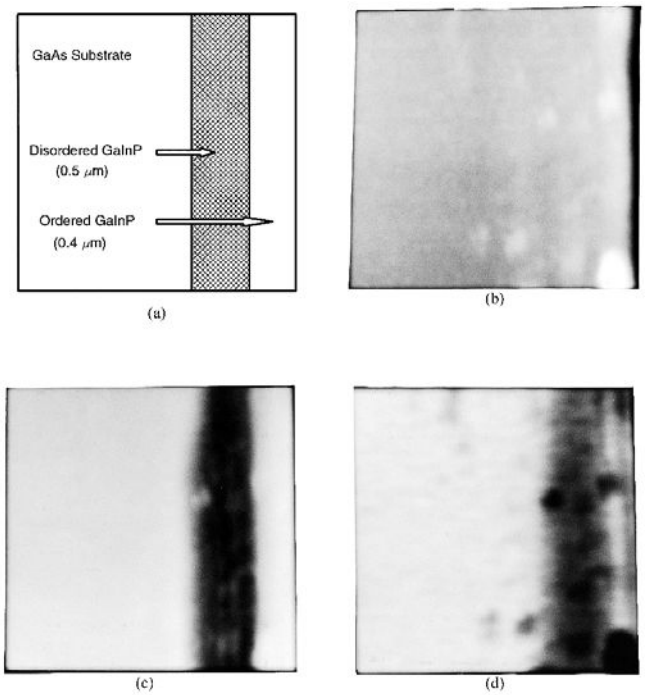

FIG. 2. (a) Schematic diagram of the order/disorder heterostructure of sample SU-10. (b), (c), and (d) are cross sectional KPFM images, with a size of 2.7 μm$\times$1.9 μm. (b) topography, (c) KPFM bucking voltage, and (d) capacitance measured at 2ω.

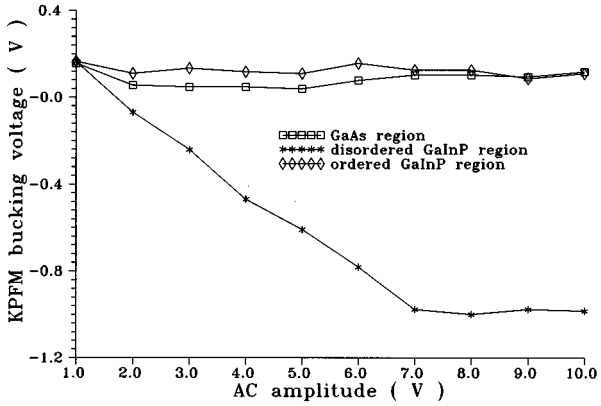

FIG. 3. KPFM bucking voltage dependence on ac amplitude in different regions of sample SU-10.

by TED and PL.[11,12] The TED patterns indicate that the bottom layer is completely disordered, and that the top layer is highly ordered.[11,12] PL measurements at high excitation intensity at a temperature of 10 K show two sharp and distinct peaks at 1.998 and 1.835 eV, which come from the disordered and ordered material, respectively.[11,12]

This sample (SU-10) was cleaved, and imaged cross-sectionally by the KPFM. Three images simultaneously obtained by the KPFM are shown in Figs. 2 (b)–2(d). Figure 2(b) represents topography, Fig. 2(c) represents KPFM bucking voltage (surface potential), and Fig. 2(d) represents capacitance measured at 2ω. The image size is 2.7 μm$\times$1.9 μm. The applied ac amplitude during imaging is 4 V. The topographic grey scale resolution is 100 nm. The dark strip on the right side of the topography image [Fig. 2(b)] indicates the edge of the cross sectional surface. Three different regions can be clearly identified in the KPFM image [Fig. 2(c)]. The middle region has a lower KPFM bucking voltage, and its thickness is about 0.5 μm. It is identified as the disordered region. The right region is the ordered GaInP. Its thickness is less than 0.4 μm, probably due to edge effects. The left region is the GaAs substrate. The capacitance image [Fig. 2(d)] also shows these three regions. The ordered GaInP and GaAs regions have about the same capacitance, while the disordered region has a smaller capacitance. The dark quasicircular spots in the capacitance image are caused by surface contamination, which are less clearly seen in the topographic image as small bumps.

It is found that the contrast between the disordered and ordered GaInP regions increases with an increase in the applied KPFM ac bias amplitude (A) [see Equation (1)]. This behavior is clearly shown in Fig. 3. The KPFM bucking voltage dependence on ac amplitude is shown with the tip in the three different regions. At low ac amplitude (1 V), there is almost no contrast among these regions. With increasing ac amplitude, the KPFM bucking voltage in the ordered layer and GaAs substrate remains almost unchanged, while it is reduced by almost 1.2 V in the disordered layer. This reduction saturates at high ac amplitude. The saturation is most likely due to the strong electrostatic force between the tip and the sample. Under this condition, the topographic feedback loop pulls the tip back with increase in applied ac bias. This has been verified by monitoring the piezo tube movement in the z direction.

A second sample (AO-98), in which ordering is controlled by the substrate misorientation, is also studied by the cross sectional KPFM. The GaInP layer was grown on a grooved GaAs (001) substrate misoriented by 9° toward $[\bar{1}10]$. The period of the groove is 40 μm, and the depth is 4 μm. The growth temperature is 670 °C, and growth rate is 2 μm/h. The thickness of the GaInP epilayer is about 5 μm. TED and CL data indicate the existence of a highly ordered $(1\bar{1}1)$ domain of several micrometer long and approximately 2 μm in thickness at the bottom of the groove close to the interface with the GaAs substrate. There exits a disordered GaInP layer about 3 μm thick on top of the ordered region.[13,14]

Images obtained in cross section by the KPFM are shown Fig. 4. A schematic drawing is shown in Fig. 4(a), with the ordered GaInP region (identified by TED and CL) indicated. Figure 4(b) represents topography obtained by the KPFM. Figures 4(c) and 4(d) are two KPFM bucking voltage images obtained with different ac biases (1 and 8 V, respectively) at the same site as Fig. 4(b). The size of three images [Figs. 4(b)–4(d)] is 14 μm$\times$13 μm. It can be clearly seen in Fig. 4(d) (8 V ac amplitude) that there is a foot shaped region at the bottom of the groove. The size of this region, as measured by the KPFM, slightly varies from groove to groove, but typically is about 2 μm wide and 8–10 μm long. This is the region which is shown to be ordered GaInP by TED and CL. In the KPFM images, this region has a surface potential very similar to the GaAs substrate. At 1 V ac amplitude [Fig. 4(c)], there is no contrast between GaAs, ordered GaInP and disordered GaInP. Surface contamination, however, can be

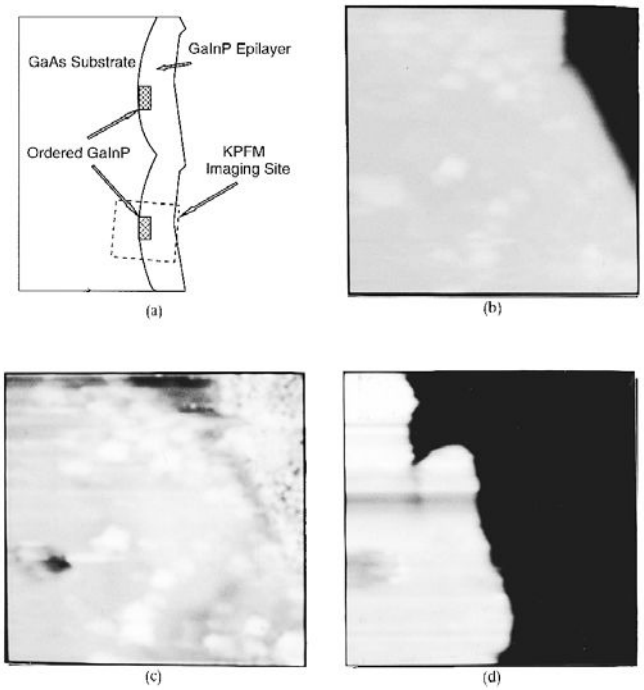

FIG. 4. (a) Schematic drawing of the groove structure of sample AO-98, (b) Topography obtained by KPFM, (c) KPFM bucking voltage image with 1 V ac amplitude, (d) KPFM bucking voltage image with 8 V ac amplitude at the same site. The size of images [(b)–(d)] is 14 μm$\times$13 μm.

identified. Figures 4(c) and 4(d) are displayed on the same grey scale.

There are several possible sources of the ac amplitude dependent contrast seen in the GaInP images. First of all, contact potential difference can be ruled out since little or no contrast is observed at low ac amplitude. It is known that because of the existence of fixed and mobile surface charge, the surface potential measured in air does not necessarily correspond to the sample work function variation.[9]

The KPFM bucking voltage dependence on ac amplitude indicates that the surface potential is influenced by the applied ac bias voltage. In the case of an uncontaminated metallic tip on an uncontaminated metallic sample, there is no such ac amplitude dependence. Our observation is that in the ordered GaInP region and GaAs region, the KPFM bucking voltage is independent of ac bias amplitude, while in the disordered GaInP region it strongly depends on ac bias amplitude. The observed KPFM bucking voltage dependence can be explained on the basis that the charging of the sample surface during the positive cycle of the applied bias is different from that during the negative cycle. This asymmetric charging will change the average potential of surface under an applied ac bias. There are several possible physical mechanisms for this.

An asymmetric carrier response to an external field in an unpinned semiconductor will result in an effective change of surface potential under an ac bias. At positive tip bias, an *n*-type semiconductor reaches accumulation, while under negative bias it goes to depletion. The surface potential change in depletion is much larger than that in accumulation. This asymmetric carrier response (as seen in MOS capacitance-voltage measurement) effectively leads to the lowering of the measured surface potential for an unpinned *n*-type semiconductor. If the surface is pinned, its potential will remain unchanged under the ac bias. Our data suggest that the surface of GaAs and ordered GaInP is pinned, while the surface of disordered GaInP is not pinned. Due to the existence of depletion in the disordered GaInP region, the measured capacitance is also expected to be smaller, as is shown in Fig. 2(d).

A second explanation for the ac amplitude dependence of the KPFM signal is that an asymmetric charge transfer may exist between the tip and sample under a symmetric ac bias. Since the electric field is rather strong between the tip and sample, (typically 10^6-10^7 V/cm), field emission may occur. The charge transfer between the tip and surface states may be asymmetric due to the non-uniform energy distribution of these states, or the inherent field emission asymmetry associated with the small tip radius. For a significant surface potential change to occur, it requires that the transferred charge stay in surface states for a time not much less than the measurement cycle (typically 1 kHz). At this point, the exact physical mechanism to explain the ac dependence of the KPFM bucking voltage has not been determined. Further study is needed.

In conclusion, ordering in GaInP, controlled by substrate misorientation and growth temperature, has been studied by the KPFM. It is shown that KPFM can visualize the difference between ordered GaInP and disordered GaInP. This contrast is found to be dependent on the applied ac amplitude used to perform the KPFM measurement. The ac amplitude dependence indicates that ordering has modified the density and/or lifetime of surface states in GaInP.

Two authors (Y.L. and C.C.W.) want to thank Y. Huang, R. Davis, A. Dicarlo, and J.K. Leong for helpful discussions. The work of the authors (L.C.S. and G.B.S.) was partially financially supported by the National Science Foundation (DMR-9320541).

[1] A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. **60**, 2645 (1988).
[2] L. C. Su, S. T. Pu, G. B. Stringfellow, J. Christen, H. Selber, and D. Bimberg, Appl. Phys. Lett. **62**, 3496 (1993).
[3] A. Gomyo, T. Suzuki, K. Kobayashi, S. Kawata, I. Hino, and T. Yuasa, Appl. Phys. Lett. **50**, 673 (1987).
[4] M. K. Lee, R. H. Horng, and L. C. Haung, Appl. Phys. Lett. **59**, 3261 (1991).
[5] D. J. Friedman, J. G. Zhu, A. E. Kibbler, J. M. Olson, and J. Moreland, Appl. Phys. Lett. **63**, 1774 (1993).
[6] D. J. Friedman, G. S. Horner, Sarah R. Kurtz, K. A. Bertness, and J. M. Olson, Appl. Phys. Lett. **65**, 878 (1994).
[7] Y. Martin, D. W. Abraham, and H. K. Wickramasinghe, Appl. Phys. Lett. **52**, 1103 (1988).
[8] M. Nonnenmacher, M. P. O'Boyle, and H. K. Wickramasinghe, Appl. Phys. Lett. **58**, 2921 (1991).
[9] K. Domansky, Y. Leng, C. C. Williams, J. Janata, and D. Petelenz, Appl. Phys. Lett. **63**, 1513 (1993).
[10] Y. Leng and C. C. Williams, Colloids Surf. (in press).
[11] L. C. Su, I. H. Ho, G. B. Stringfellow, Y. Leng, and C. C. Williams, Mater. Res. Soc. Symp. Proc. **340**, 123 (1994).
[12] L. C. Su, I. H. Ho, and G. B. Stringfellow, Appl. Phys. Lett. **65**, 749 (1994).
[13] A. Krost, N. Esser, H. Selber, J. Christen, W. Richter, D. Bimberg, L. C. Su, and G. B. Stringfellow, J. Vac. Sci. Technol. B **12**, 2558 (1994).
[14] A. Krost, N. Esser, H. Selber, J. Christen, W. Richter, D. Bimberg, L. C. Su, and G. B. Stringfellow, J. Cryst. Growth (in press).