Interface structure and chemistry in $ZnSe/Ga_{1-x}Mn_xAs/ZnSe$ heterostructures

G. D. Lian and E. C. Dickey[a)]
Department of Materials Science and Engineering and the Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

S. H. Chun,[b)] K. C. Ku, and N. Samarth
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 12 December 2002; accepted 31 March 2003)

The structure and chemical composition of $ZnSe/Ga_{1-x}Mn_xAs/ZnSe$ multilayers grown on (100) GaAs substrates are investigated by high-resolution transmission electron microscopy imaging and spectroscopy techniques. While all layers grow epitaxially and the $Ga_{1-x}Mn_xAs$ layer is free of planar defects, a high density of stacking faults is observed in the ZnSe layer over $Ga_{1-x}Mn_xAs$. The composition of the ferromagnetic layer is measured to be $Ga_{0.93}Mn_{0.07}As$, and the Mn valence was determined to be 2^+. Compositional profiles across the interfaces quantified by electron energy-loss spectroscopy show that the $ZnSe/Ga_{1-x}Mn_xAs$ interfaces are wider than the ZnSe/GaAs–substrate interface, which is mainly attributed to interfacial roughness. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1577825]

There is substantial contemporary interest in exploiting both the charge and spin of electrons in semiconductor ''spintronic'' devices.[1,2] In order to develop prototype devices, it is important to first explore the epitaxial growth of hybrid ferromagnet/semiconductor heterostructures wherein conventional semiconductors such as GaAs are combined with ferromagnetic semiconductors such as $Ga_{1-x}Mn_xAs$. However, the molecular-beam epitaxy (MBE) growth of ferromagnetic $Ga_{1-x}Mn_xAs$ requires a significantly lower substrate temperature (~250 °C) than that typically used for the growth of high quality GaAs. Since the temperature of a $Ga_{1-x}Mn_xAs$ layer cannot be raised above 300 °C without creating metallic inclusions of MnAs, the overgrowth of high quality GaAs is not possible. This sets severe constraints on the design of complex ferromagnet/semiconductor heterostructures derived from III–V semiconductors alone.

As an alternative, we have proposed the development of hybrid II–VI/III–Mn–V heterostructures such as $ZnSe/Ga_{1-x}Mn_xAs$.[3] This material system offers a possible route towards epitaxially grown device configurations such as heterojunction bipolar spin transistors, since the optimal growth conditions for the different material components are compatible. In order to advance the fabrication of such devices, it is crucial to obtain detailed microscopic characterization of the interfacial structure.

Here, we use a variety of electron microscopy techniques to analyze the interfacial structures and chemistries of MBE-grown *n*-ZnSe/*p*-$Ga_{1-x}Mn_xAs$/*n*-ZnSe heterostructures. Although high-resolution transmission electron microscopy (HRTEM) has been used extensively for studying the ZnSe/GaAs interface created by epitaxial growth of ZnSe on GaAs,[4–7] there has been very little work on the inverse case.[8] Our results provide experimental measurements of elemental distributions across these interfaces at subnanometer resolution. Such information regarding the interface chemical abruptness could be important for interpreting experiments that study spin transport across interfaces.[9] We find that, even though HRTEM indicates coherent interfaces between ZnSe and $Ga_{1-x}Mn_xAs$ (similar to those observed in earlier studies[4–8] of ZnSe/GaAs), electron energy-loss spectroscopy (EELS) reveals a chemical width up to ~4 nm along the growth axis. We attribute these broad chemical profiles primarily to interfacial roughness. These results indicate limitations in the interfacial quality of such hybrid heterostructures.

The samples were grown by MBE on (100) semi-insulating GaAs substrates, as detailed elsewhere.[3] In brief, after growing a 350-nm ZnSe layer at 250 °C on a (100) GaAs substrate, the substrate temperature was lowered to 20 °C, and about two monolayers of amorphous GaAs were deposited. This amorphous layer was recrystallized[8] when the substrate temperature was raised to 250 °C for the growth of 50 nm of $Ga_{1-x}Mn_xAs$ with x nominally equal to 0.05. This was followed by the growth of a 350-nm ZnSe layer at the same temperature. For cross-sectional HRTEM specimen preparation, two thin slices of the heterostructure were glued together with *M*-bond 610. The sections were polished to about 10 μm using a tripod polisher and diamond-embedded lapping films, followed by ion milling at liquid nitrogen temperature with successively decreasing ion beam voltage. This method has been shown to minimize ion beam damage in ZnSe.[4,5] Structural characterization and chemical analysis were carried out on a JEOL 2010F field-emission transmission electron microscope (TEM)/scanning-TEM (STEM), equipped with an annular dark-field detector and post-column EELS image filter (Gatan GIF200). In order to collect both the Zn $L_{2,3}$ and Se $L_{2,3}$ in one spectrum, 1 eV per channel dispersion was used and the energy resolution was ~2 eV. The EEL spectra were collected and analyzed using

a)Author to whom correspondence should be addressed; electronic mail: ecd10@psu.edu
b)Present address: Department of Physics, Sejong University, Seoul 143-747, Korea.

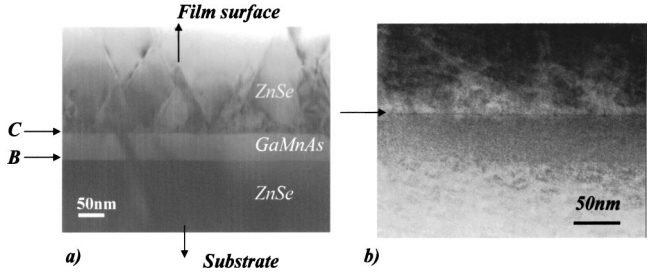

FIG. 1. (a) Bright-field TEM image shows ZnSe/$Ga_{1-x}Mn_xAs$/ZnSe multilayers. Interface A is ZnSe/GaAs–substrate (not shown here), B and C are the interfaces of ZnSe/$Ga_{1-x}Mn_xAs$/ZnSe, as marked in the figure. Stacking faults are observed at interface C. (b) Annular dark-field STEM image of the interfaces that shows a dark line at interface C, as marked by the arrow.

ELP in a digital micrograph (Gatan, Inc.) to quantify the composition of the thin films.

Figure 1(a) is a bright-field TEM image from the cross section showing the two interfaces about the $Ga_{1-x}Mn_xAs$ layer. The interfaces are identified as A (ZnSe over GaAs substrate, not shown), B ($Ga_{1-x}Mn_xAs$ over ZnSe), and C (ZnSe over $Ga_{1-x}Mn_xAs$). Both the $Ga_{1-x}Mn_xAs$ layer and interface B are defect free. However, a high density of planar defects is clearly evidenced in the upper ZnSe layer and at interface C. These defects were identified as stacking faults, which are frequently observed in the epitaxial growth of ZnSe on GaAs and can be related to the formation of a Ga–Se vacancy ordering at the interface, which provides nucleation centers for stacking faults.[6,7] Figure 1(b) shows a *Z*-contrast STEM image of the same interfaces, in which the intensities correspond to the approximately the square of the average projected atomic number.[10–12] The dark line observed at interface C may be evidence of the relatively low atomic number Ga–Se vacancy ordering layer. The defect-free $Ga_{1-x}Mn_xAs$/ZnSe interface (B) and $Ga_{1-x}Mn_xAs$ layer can be attributed to the enhancement in sticking coefficient of As_4 on the Zn-terminated ZnSe surface by deposition of amorphous GaAs at room temperature prior to the $Ga_{1-x}Mn_xAs$ growth. The other related factor is that the thickness of $Ga_{1-x}Mn_xAs$ is well below the critical thickness, above which misfit dislocations are generated.

Figure 2 shows HRTEM images of the two ZnSe/$Ga_{1-x}Mn_xAs$ interfaces and the underlying ZnSe/GaAs–substrate interface projected along the [001] zone axis, which is the most chemically sensitive HRTEM imaging condition for revealing the interface between two zinc-blende structured materials.[13] Epitaxial and coherent interfaces are evident in all cases. The observed fluctuations in the lattice contrast at interfaces could be due to Se diffusion into GaAs or $Ga_{1-x}Mn_xAs$[6] or to interfacial roughness. It is qualitatively apparent from the HRTEM contrast that ZnSe/GaAs–substrate interface is more abrupt than either ZnSe/$Ga_{1-x}Mn_xAs$ interface; however, we quantitatively measure the interface width via EELS, as described subsequently.

Figure 3 presents EEL spectra collected from the ZnSe and $Ga_{1-x}Mn_xAs$ layers, which show the characteristic $L_{2,3}$ ionization edges from GaAs and ZnSe. The inset is the Mn $L_{2,3}$ edge acquired from the $Ga_{1-x}Mn_xAs$ layer. Using Hartree–Slater scattering cross sections, the concentration of Mn in $Ga_{1-x}Mn_xAs$ was quantified to be $x=0.07\pm0.01$.

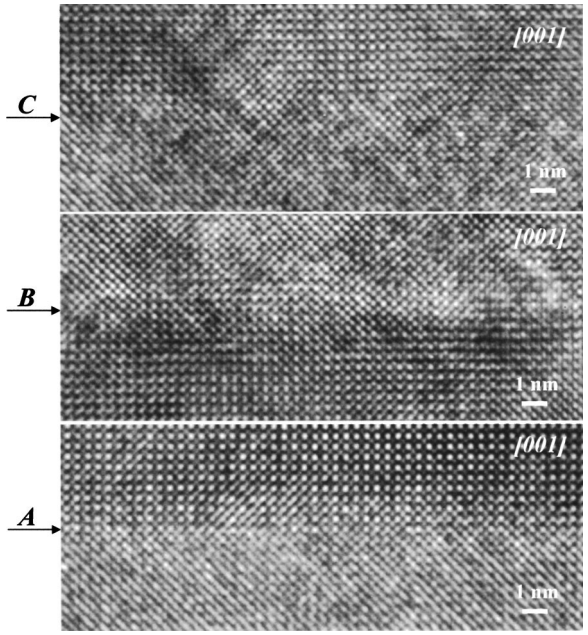

FIG. 2. HRTEM images showing interfaces (A) ZnSe/GaAs–substrate, (B) $Ga_{1-x}Mn_xAs$ on ZnSe, and (C) ZnSe on $Ga_{1-x}Mn_xAs$.

Detailed analysis of the Mn $L_{2,3}$ edge fine structure shows the L_3/L_2 ratio is 7.2, consistent with a 2^+ valence state,[14] confirming the acceptor behavior of Mn^{2+} to provide both holes and magnetic moment.

In order to examine the chemical abruptness of the interfaces, EEL spectra were collected using a 0.5-nm electron probe stepped across the interfaces in 0.5-nm steps. The edge overlaps made it difficult to quantify the concentration distribution at the interface region by conventional EELS analysis. Therefore, a multiple least-squares fitting method[15,16] was used to quantify the elemental concentrations from the spectra. For this purpose, a Ga reference spectrum was obtained from GaN, and an As reference spectrum was collected from InAs. No appreciable changes in the fine structures of the edges were observed between the reference and GaAs spectra. Since the $L_{2,3}$ edges of Zn and Se are well separated, the Zn and Se reference spectra were acquired from the ZnSe layer far away from the interfaces.

The chemical width of the interface was defined as the

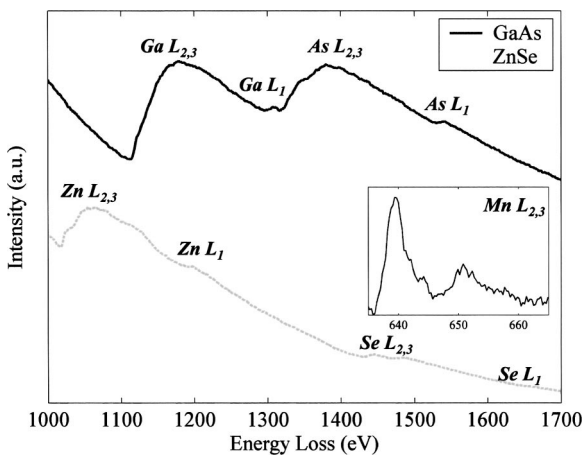

FIG. 3. Typical EEL spectra taken from $Ga_{1-x}Mn_xAs$ and ZnSe layers. Inset is Mn $L_{2,3}$ edge obtained from the $Ga_{1-x}Mn_xAs$ layer.

TABLE I. Interfacial chemical widths as measured by EELS (in nm).

Element	ZnSe/GaAs–substrate (A)	$Ga_{1-x}Mn_xAs$/ZnSe (B)	ZnSe/$Ga_{1-x}Mn_xAs$ (C)
Zn	1.6	3.8	3.6
Se	1.5	4.1	3.4
Ga	1.7	4.1	3.6
As	1.5	3.5	3.5

range over which the concentration changed from 10% to 90% of the bulk concentration, and the results for each interface are presented in Table I. The chemical width of the ZnSe/GaAs–substrate interface is about 1.5 nm. Considering that the electron probe size was 0.5 nm at full width at half-maximum, the profile of a perfect step-function would lead to a measured chemical width of 1.2 nm, assuming a Lorentzian probe shape. Therefore, the profile from the ZnSe/GaAs–substrate interface (A) is consistent with a nearly atomically abrupt interface, with intermixing confined to two monolayers. EELS profiles across the ZnSe/$Ga_{1-x}Mn_xAs$/ZnSe interfaces (B and C) are significantly broader, averaging ~4 nm. The broadening is well above the inherent spatial resolution of the EELS profiles and indicates a more diffuse interface over the length scale of several nanometers. We believe that this measured chemical thickness arises mainly from the rough growth front of these layers and is not necessarily an interdiffusion effect. First of all, similar interdiffusion would have been expected at the ZnSe/GaAs–substrate interface since all interfaces had similar thermal histories and are chemically similar. Moreover, we found a correlation between the interface width and specimen thickness across both ZnSe/$Ga_{1-x}Mn_xAs$ interfaces, ranging from ~5 nm in the thickest samples to a minimum of ~3 nm in the thinnest samples. The surface roughness of ZnSe grown on GaAs has previously been measured to be up to 4 nm rms,[17] which could explain most of the width in the measured profiles.

In summary, the detailed structure and chemical composition of *n*-ZnSe/*p*-$Ga_{1-x}Mn_xAs$/*n*-ZnSe heterostructures were analyzed using HRTEM, *Z*-contrast STEM imaging, and EELS. Although all layers were epitaxial, a high density of stacking faults was found in the ZnSe layer over $Ga_{1-x}Mn_xAs$, whereas the $Ga_{1-x}Mn_xAs$ layer was defect free. Both the concentration and valence state of Mn in the $Ga_{1-x}Mn_xAs$ layer were quantified from EELS, yielding $x=0.07$ and a valence of 2^+. The chemical abruptness of the interfaces was quantified by EELS, and the relatively broad ZnSe/$Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs$/ZnSe interface profiles were attributed mainly to interfacial roughness.

This work was supported by Grant Nos. ONR N00014-99-1-0071, -0716, and DARPA/ONR N00014-99-1-1093.

[1] S. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science (Washington, DC, U.S.) **294**, 1488 (2001).
[2] *Semiconductor Spintronics and Quantum Computation*, edited by D. D. Awschalom, D. Loss, and N. Samarth (Springer, Berlin, 2002).
[3] S. H. Chun, K. C. Ku, S. J. Potashnik, P. Schiffer, and N. Samarth, J. Vac. Sci. Technol. B **20**, 1266 (2002).
[4] N. G. Chew and A. G. Cullis, Ultramicroscopy **23**, 175 (1987).
[5] N. Wang and K. K. Fung, Ultramicroscopy **60**, 427 (1995).
[6] T. Walter and D. Gerthsen, Ultramicroscopy **81**, 279 (2000); K. Ueno, M. Kawayama, Z. R. Dai, A. Koma, and F. S. Ohuchi, J. Cryst. Growth **207**, 69 (1999).
[7] L. H. Kuo, K. Kimura, T. Yasuda, S. Miwa, C. G. Jin, and K. Tanaka, Appl. Phys. Lett. **68**, 2413 (1996).
[8] S. Ramesh, N. Kobayashi, and Y. Horikoshi, Appl. Phys. Lett. **57**, 1102 (1990).
[9] I. Malajovich, J. J. Berry, N. Samarth and D. D. Awschalom, Nature (London) **411**, 7070 (2001).
[10] S. J. Pennycook and D. E. Jesson, Phys. Rev. Lett. **64**, 938 (1990).
[11] S. J. Pennycook and D. E. Jesson, Ultramicroscopy **37**, 14 (1991).
[12] P. D. Nellist and S. J. Pennycook, Ultramicroscopy **78**, 111 (1999).
[13] A. Ourmazd, D. W. Tayler, M. Bode, and Y. Kim, Science (Washington, DC, U.S.) **246**, 1571 (1989).
[14] H. Kurata and C. Colliex, Phys. Rev. B **48**, 2102 (1993).
[15] R. D. Leapman and J. A. Hunt, Microsc. Microanal. Microstruct. **2**, 231 (1991).
[16] F. Hofer and G. Kothleitner, Microsc. Microanal. Microstruct. **4**, 539 (1993).
[17] J. J. Berry, R. Knobel, O. Ray, W. Peoples, and N. Samarth, J. Vac. Sci. Technol. B **18**, 1692 (2000).