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Atomic scale characterization of Mn doped InAs/GaAs quantum dots

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Several growth procedures for doping InAs/GaAs quantum dots (QDs) with manganese (Mn) have been investigated with cross-sectional scanning tunneling microscopy. It is found that expulsion of Mn out of the QDs and subsequent segregation makes it difficult to incorporate Mn in the QDs even at low growth temperatures of T=320 °C and high Mn fluxes. Mn atoms in and around QDs have been observed with strain and potential confinement changing the appearance of the Mn features. © *2010 American Institute of Physics*. [doi:10.1063/1.3293296]

Diluted magnetic semiconductors (DMSs) such as GaMnAs have attracted a lot of attention in the past decade because of their interesting magnetic properties and their potential applications in future devices. The origin of ferromagnetism in bulk GaMnAs is attributed to the *p-d* exchange between the electrons populating a half filled *d*-shell of the Mn atoms and the *p*-like valence band holes of the Mn acceptor. Therefore DMS nanostructures such as Mn doped InAs/GaAs quantum dots (QDs) are expected to exhibit magnetic, electronic and optical properties making them interesting as building blocks for spintronic devices utilizing the quantized properties of the charge carriers confined in them. The fact that these nanostructured spintronic devices can be electronically and optically active as well makes them even more attractive. The most spectacular work in this field concerns the analysis of QDs doped with a single magnetic impurity.[1,2] The growth of magnetic II/VI QDs is well established in contrast to the situation for III/V magnetic QDs. Although several groups[3–6] have reported on the growth of Mn doped InAs QDs in GaAs there is hardly any evidence that these Mn doped structures are truly magnetically active and that Mn is incorporated in the structures. Although many characterization techniques have been employed to study these magnetically doped dots the research is severely hampered by the lack of a proper technique to visualize the incorporation of Mn in InAs QDs. This lack of high resolution data often leads to a high degree of speculation in the interpretation. In the past we have used cross-sectional scanning tunneling microscopy (X-STM) to image the structural properties of individual QDs.[7] The same technique was used by us to analyze individual Mn impurities in detail[8] and thus X-STM is an ideal tool to study the incorporation of Mn in InAs QDs. Such analysis should be able to resolve several controversies that exist in this young field of the growth of magnetic III/V QDs. It is, for example, still not clear whether

Mn acts as a surfactant or as nucleation point for QD formation.[4,5] Also on other issues like the influence of Mn doping on PL emission of QDs, different experiments[9–11] obtained contradicting results. This makes an analysis of Mn doped QDs at atomic scale necessary. In this letter, X-STM results on Mn doped InAs/GaAs QDs are reported. Emphasis is put on the incorporation mechanism rather than the behavior of the Mn acceptor inside the QD.

The experiments have been performed on three sets of samples which will be called set A, B, and C. They are all grown with molecular beam epitaxy (MBE) on (001) GaAs n-type substrates. The two-dimensional–three-dimensional transition related to QD formation was monitored with reflection high-energy electron diffraction. For the first two sets, the growth temperature was measured carefully with a BandiT[12] system. For the third set, the temperature was monitored by a thermocouple and a pyrometer.

Set A was designed to find a suitable growth procedure to incorporate as many Mn atoms as possible in the InAs QDs. This set consisted of four wafers in which the Mn has been incorporated in the InAs QDs in four different ways; Mn deposition on the GaAs surface prior to the growth of 2.1 ML of InAs, the growth of 0.1 ML of InMnAs followed by 2.0 ML of InAs, the growth of 0.1 ML of InMnAs sandwiched between two 1.0 ML of InAs layers and finally termination of the GaAs buffer layer with GaMnAs before 2.1 ML of InAs was deposited. The growth temperature for set A was put at T=450 °C to limit segregation and still obtain optically active QDs. The total amount of deposited Mn in all four cases was about 10^{11} cm^{-2} corresponding to 0.016%. The same MBE setup was used to grow set B which was designed to characterize the segregation behavior of Mn δ-layers in GaAs at temperatures of T=350 and T=400 °C.

Set C was grown in a different MBE setup where more extreme conditions were used to incorporate Mn in InAs QDs. In this sample, six QD layers were grown with intended amounts of Mn ranging from 0% to 5% at a further reduced growth temperature of T=320 °C. A total of 2.4 ML of InAs was deposited to form the QD layer with the Mn cell open only during the deposition of the last 1.4 ML of InAs.

Before the X-STM measurements, the samples are cleaved under UHV ($p \approx 4 \times 10^{-11}$ Torr) conditions and the
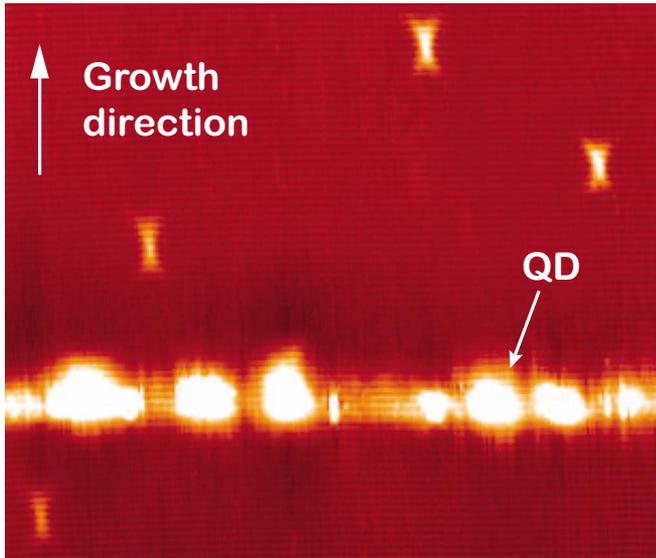

FIG. 1. (Color online) Typical X-STM image obtained on one of the samples from set A. The image is taken at V=+1.5 V and I=32 pA and size of the image is 43×79 nm.

cleaved [110] surface is scanned at room temperature or 77 K with a polycrystalline tungsten tip. The optimal imaging conditions for Mn acceptors in GaAs occur at positive voltages of 1.0 to 1.5 V applied to the sample.

In Fig. 1 a typical image of a sample from set A is shown. The QD size and shape are poorly defined due to the low growth temperature. The Mn atoms in the image, recognizable by their characteristic bowtie shape,[8] have segregated in the growth direction. Only occasionally, Mn atoms are observed in the wetting layer and no cases were found where a Mn atom is visible inside the QD. A similar behavior was found in all the respective samples in set A. Thus irrespective of the growth procedure of the samples in set A, segregation of the Mn atoms dominates the Mn distribution and consequently limits the incorporation of Mn in the QD layer.

Because of the high resolution of X-STM, we were able to study the Mn distribution in more detail. In Fig. 2, Mn distribution profiles are shown which were obtained on
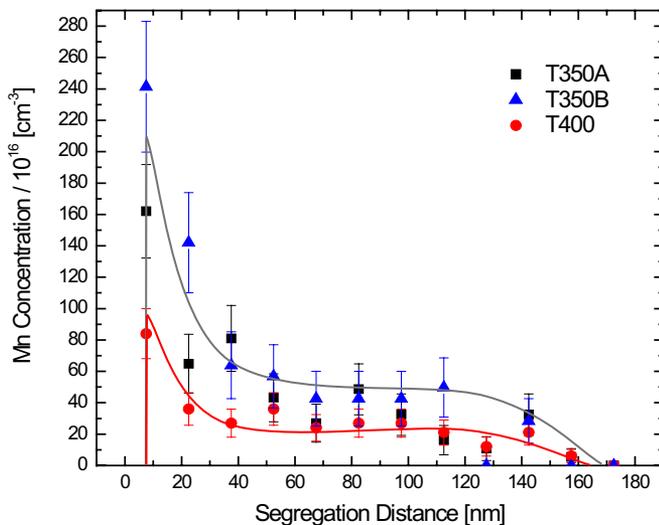

FIG. 2. (Color online) Segregation graphs for different temperatures. The lines for T350 and T400 are not actual fits but general indications of the segregation behavior.

samples from set B. The profiles for the two different growth temperatures show a similar fast decay in the Mn distribution in the layers immediately above the intended doping layer. This fast decay ends at about 40 nm away from the intended doping layer. In the interval ranging from 40 nm to 150 nm the Mn concentration is constant and finally drops to zero beyond this interval. The relatively fast decay is related to segregation of the deposited Mn as reported before.[13] The second part of the profile with the constant Mn concentration is probably caused by Mn desorption from the sample holders and walls of the growth chamber and subsequent deposition on the sample. This memory effect of the growth chamber stops after the growth of about 150 nm GaAs which corresponds to approximately 25 min growth time after the Mn cell was opened. It must be noted that the amount of Mn in this second part of the graph is below the SIMS detection limit.[14] Furthermore, the lower concentration of Mn at a growth temperature of T=400 °C compared to a growth temperature of T=350 °C is probably due to Mn desorption from the growth front which is more important at higher growth temperatures.

In order to maximize the Mn incorporation in InAs QDs it is very important that segregation is minimized even further by decreasing the growth temperature. Furthermore, we have increased the doping concentration considerably. The low growth temperature is however a major problem for the quality of the grown QDs. Lower temperatures result in smaller less well defined QDs having a larger number of internal defects causing very poor optical properties. Nevertheless the samples of set C are grown at a temperature of 320 °C. In this sample the total amount of deposited InAs is 2.4 ML and the intended Mn doping is increased stepwise up to 5%.

In the samples of set C we observed that even at T=320 °C, segregation of Mn in the growth direction is very important. However because of the high amount of Mn deposited, the chance of finding a Mn atom inside a QD is highly improved. In Fig. 3, a topographic image and the current image (which resembles a spatial derivative of the topography image) of a QD with several Mn atoms in and around it are shown. Mn features are indicated by the characters A to E.

The Mn feature A represents an example of a single Mn atom in GaAs. The bowtie shape of the deep Mn acceptor in bulk GaAs with a binding energy of 113 meV is well understood[8] and is due to the charge distribution of the hole bound to the Mn acceptor. Similar features have been observed in Mn doped InAs[15] where Mn behaves as a shallow acceptor with a binding energy of about 28 meV. Feature B represents a Mn atom in the wetting layer and its shape seems to be marginally affected by the strain and confinement potential of the InGaAs wetting layer. Mn C is located exactly at the interface of the InAs QD and the GaAs matrix. The contrast of a Mn atom at the interface shows part of the bowtie in the GaAs area whereas the contrast in the QD is absent. It is not yet clear why the Mn contrast is absent in the QD. We observed that the number of Mn atoms residing at the interface is far larger than the number of Mn atoms in the QD. We think that this is related to the formation energy for the incorporation of a Mn acceptor in an InAs nanostructure as calculated by a DFT method.[16] These calculations show that the formation energy also increases for smaller InAs nanocrystals (300→500 meV). We suggest that this forma-
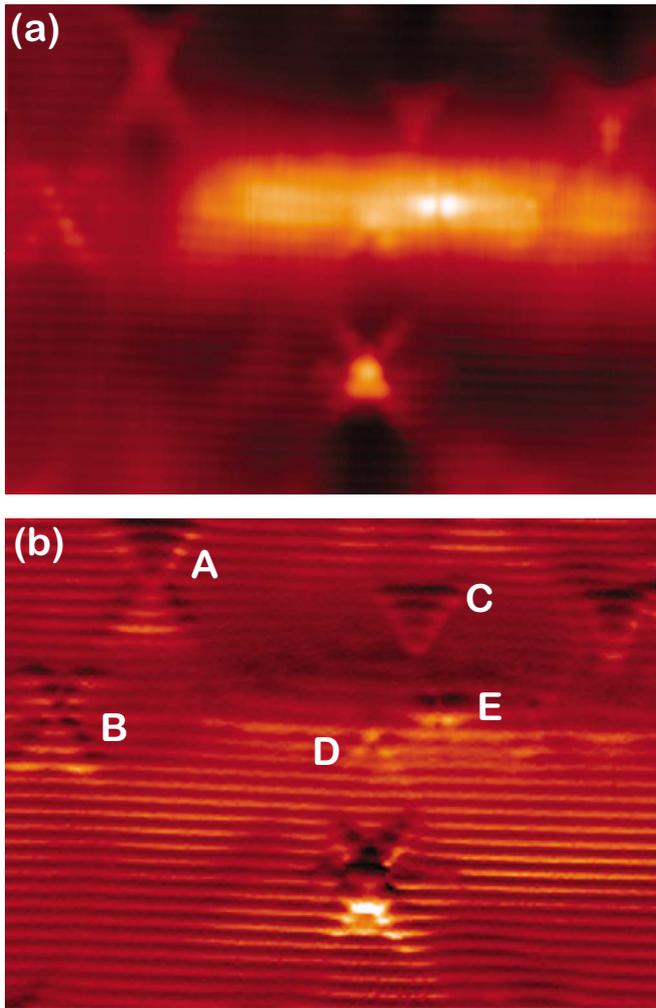
FIG. 3. (Color online) Topography (a) and current (b) image of Mn atoms at different positions in and around a QD from layer 6 with 5% intended amount of Mn. Image taken at V=+1.45 V and I=15 pA. Size of the image is 18×29 nm.

ficult to explain at the moment why we see these specific Mn features in the dot. The same applies for the missing part of wave function in the dot for Mn atoms at the InAs/GaAs interface of the dot.

In conclusion, we have shown that Mn segregation is a major problem which strongly limits the incorporation of Mn atoms in a QD. Even at a low growth temperature of T =320 °C segregation still dominates the Mn distribution. However in strongly doped structures we have observed large numbers of Mn acceptors present in the wetting layer and a limited number of Mn atoms in a QD. Mn incorporation in QDs is possibly further complicated by strain induced segregation toward the InAs surface of the QD.

tion energy drives Mn atoms toward the QD interface. Next to segregation this process further complicates the Mn doping of QDs. The Mn features D and E are related to Mn acceptors in the QD. Their contrast is strongly modified compared to Mn in GaAs. Several mechanisms such as strain,[17] potential confinement and position near to the cleaved surface[18] are expected to have an impact on the wave function of the Mn acceptor. Unfortunately within a QD all these mechanisms play a complicated role and thus it is very dif-

[1]L. Besombes, Y. Léger, L. Maingault, D. Ferrand, J. Cibert, and H. Mariette, Physica E **35**, 300 (2006).
[2]A. Kudelski, A. Lemaître, A. Miard, P. Voisin, T. C. M. Graham, R. J. Warburton, and O. Krebs, Phys. Rev. Lett. **99**, 247209 (2007).
[3]M. Holub, S. Chakrabarti, S. Fathpour, P. Bhattacharya, Y. Lei, and S. Ghosh, Appl. Phys. Lett. **85**, 973 (2004).
[4]S. P. Guo, A. Shen, H. Yasuda, Y. Ohno, F. Matsukura, and H. Ohno, J. Cryst. Growth **208**, 799 (2000).
[5]Y. K. Zhou, H. Asahi, J. Asakura, S. Okumura, K. Asami, and S. Gonda, J. Cryst. Growth **221**, 605 (2000).
[6]Y. K. Zhou, H. Asahi, J. Asakura, S. Okumura, T. Tashima, J. Sato, K. Asami, and S. Gonda, Physica E (Amsterdam) **7**, 1001 (2000).
[7]J. H. Blokland, M. Bozkurt, J. M. Ulloa, D. Reuter, A. D. Wieck, P. M. Koenraad, P. C. M. Christianen, and J. C. Maan, Appl. Phys. Lett. **94**, 023107 (2009).
[8]A. M. Yakunin, A. Yu. Silov, P. M. Koenraad, J. H. Wolter, W. Van Rooy, J. De Boeck, J.-M. Tang, and M. E. Flatté, Phys. Rev. Lett. **92**, 216806 (2004).
[9]O. V. Vikhrova, Yu. A. Danilov, Yu. N. Drozdov, B. N. Zvonkov, F. Iikawa, and M. J. S. P. Brasil, J. Surface Invest. X-ray, Synchrotron, and Neutron Tech. **1**, 64 (2007).
[10]L. J. Hu, Y. H. Chen, X. L. Ye, X. Q. Huang, L. Y. Liang, F. Ding, and Z. G. Wang, Physica E (Amsterdam) **36**, 221 (2007).
[11]P. J. Wellmann, W. V. Schoenfeld, J. M. Garcia, and P. M. Petroff, J. Electron. Mater. **27**, 1030 (1998).
[12]C. T. Foxon, R. P. Campion, V. A. Grant, S. V. Novikov, J. J. Harris, R. Thomson, C. Taylor, and D. Barlett, J. Cryst. Growth **301**, 482 (2007).
[13]J. J. Harris, D. E. Ashenford, C. T. Foxon, P. J. Dobson, and B. A. Joyce, Appl. Phys. A: Mater. Sci. Process. **33**, 87 (1984).
[14]A. M. Nazmul, S. Sugahara, and M. Tanaka, J. Cryst. Growth **251**, 303 (2003).
[15]F. Marczinowski, J. Wiebe, J.-M. Tang, M. E. Flatté, F. Meier, M. Morgenstern, and R. Wiesendanger, Phys. Rev. Lett. **99**, 157202 (2007).
[16]J. T. Arantes, G. M. Dalphian, and A. Fazzio, Phys. Rev. B **78**, 045402 (2008).
[17]A. M. Yakunin, A. Yu. Silov, P. M. Koenraad, J.-M. Tang, M. E. Flatté, J.-L. Primus, W. Van Roy, J. De Boeck, A. M. Monakhov, K. S. Romanov, I. E. Panaiotti, and N. S. Averkiev, Nature Mater. **6**, 512 (2007).
[18]J. K. Garleff, C. Çelebi, W. Van Roy, J.-M. Tang, M. E. Flatté, and P. M. Koenraad, Phys. Rev. B **78**, 075313 (2008).