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Attractive interaction between Mn atoms on the GaAs(110) surface observe by scanning tunneling microscopy

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Scanning tunneling microscopy/spectroscopy (STM/STS) was carried out to investigate the structures of Mn atoms deposited on a GaAs(110) surface at room temperature to directly observe the characteristics ofi nteractions between Mn atoms in GaAs. Mn atoms were paired with a probability higher than the random distribution, indicating an attractive interaction between them. In fact, re-pairing of unpaired Mn atoms was observed during STS measurement. The pair initially had a new structure, which was transformed during STS measurement into one of those formed by atom manipulation at 4 K. Mn atoms in pairs and trimers were aligned in the <110> direction, which is theoretically predicted to produce a high Curie temperature.

Over the past few decades, diluted magnetic semiconductors (DMSs), in which some atomic sites in a host semiconductor are substituted by transition metal atoms, have been energetically studied to provide prospective materials for application to spintronics, because they are compatible with general semiconductor devices.[1,2] Control of the spatial distribution of transition-metal atoms in a DMS is a key factor in realizing desirable magnetic characteristics. Several papers have reported such control by carrier doping for DMSs such as (Zn, Cr)Te and GeMn.[1–3] In these studies, the spatial distributions of transition-metal atoms were varied by changing the polarity of the host semiconductors; for example, for (Zn, Cr)Te,[3] Cr atoms were aggregated by donor doping and strongly interacted with each other by ferromagnetic coupling, which may result in a ferromagnetic transition temperature higher than room temperature (RT). For further advances, however, it is necessary to understand such interactions in detail and the characteristics of their atomic structures.

(Ga, Mn)As is one of the fundamental and well-studied ferromagnetic DMSs.[2,4] In (Ga, Mn)As, Mn dopants, which substitute Ga sites, act as not only magnetic impurities but also acceptors generating holes. Since a (Ga, Mn)As sample with a high hole concentration realizes a high ferromagnetic transition temperature (Curie temperature: T_c), the model of carrier-mediated ferromagnetism has been proposed and widely accepted as the origin of the ferromagnetic character observed for (Ga, Mn)As.[5] However, the highest T_c experimentally achieved so far for (Ga, Mn)As is about 200 K, which is still low for practical applications.[6–8] According to theoretical and experimental studies,[9–12] the ferromagnetic interaction between two transition metal atoms changes with their ordering direction and the distance of the neighbouring atoms. The ordering of the nearest-neighbouring Mn atoms in a pair along the <110> direction is expected to achieve the strongest ferromagnetic interaction.[9,13] Hence, if we can control Mn atoms to align along the <110> direction, we may realize a (Ga, Mn)As sample with a higher T_c.

Such magnetic interactions between Mn atoms, which depend on the atom arrangements, were experimentally studied by Kitchen et al. by scanning tunneling microscopy and spectroscopy (STM/STS).[10,11] They fabricated structures of Mn pairs by STM atom manipulation at 4 K and investigated their ferromagnetic interactions by observing the splitting of Mn acceptor levels which reflects the degree of bonding and antibonding state formation. And thus, they reported results similar to that predicted by theoretical study. However, since these structures were artificially fabricated at 4 K, understanding of the characteristics of natural structures in the interaction between transition metals is necessary.

Here, we present the STM/STS results obtained for the Mn structures deposited on a GaAs(110) surface at room temperature (RT) showing attractive interaction between Mn atoms aligned in the <110> direction; this suggests the possibility of self-arrangement of Mn atoms to produce a higher T_c.

A clean GaAs(110) surface was prepared by cleaving a GaAs sample in an ultrahigh vacuum of 1×10^{-6} Pa. Mn atoms were deposited on the GaAs(110) surface at RT by using an e-beam evaporator. All STM/STS measurements were carried out at RT using an Omicron variable-temperature STM system. I–V characteristics were probed by changing the bias voltage from −1.8 V to +1.5 V at 27 × 27 mesh points in each scan area along with simultaneous STM imaging with the set point of bias voltage and tunneling current of (V_s, I_t) = (−1.5–2.0 V, 0.05–0.20 nA).

According to Kitchenet al., Mn atoms deposited at 4 K form pairs without manipulation for an n-type sample, and thus they carried out an experiment using a p-type sample that did not exhibit any pairing.[10,11] To clarify this point, we carried out experiments on both p- and n-type samples.

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Fig. 1(a) and (b) show STM images of p-type (Zn-doped, 1–5 × 10^{17} cm^{-3}) and n-type (Si-doped, 1–5 × $10^{17}cm^{-3}$) GaAs(110) sample surfaces with Mn atoms deposited on them, respectively. Single, pair, and trimer Mn structures are labelled S, P, and T in the figure, respectively, and their magnified images are shown together on the right side of the wide-scan images. Fig. 1(c) and (d) show the spectra obtained above a bare GaAs surface and the structures of S and P for p- and n-type samples, respectively. There is a signal peak at~0.8 V for S, and an earlier increasing characteristic was observed for P in comparison with the spectrum obtained for a bare GaAs surface. The apparent difference in the negative sample bias voltage region observed between the spectra of p- and n-type samples is due to the difference in the Fermi energy position, as schematically shown in Fig. 1(e) (shown for a positive bias voltage here),[14] and the additional tunneling of electrons from the valence band through the Mn acceptor level for the case of the p-type sample at negative bias voltages.

Fig. 1(f) shows the histogram of the Mn structures obtained from the total count of 300 structures for each of the p- and n-type surfaces. The ratios of Mn pairs to single Mn atoms were 20% and 29% for p- and n-types, respectively, which are higher than those expected from the random distribution, 0.8% and 1.4% for p- and n-types, respectively. The random distribution was estimated by the equation: $1-(1-x)^n$, where x is the Mn concentration obtained from STM images, 0.4% for p-type and 0.7% for n-type, and n is the number of the nearest neighbouring sites, 2 for this case. These results indicate that there exists an attractive interaction between Mn atoms on the GaAs(110) surface. The results were almost the same between the p- and n-type samples. The slight difference in the possibility of pairing observed between the p- and n-type samples may be related to the fact that pair structures without manipulation at 4 K were observed only for the n-type surface, as mentioned in the work by Kitchen. [11] Since a Mn atom placed at a Ga site acts as an acceptor, such a replacement may be suppressed for

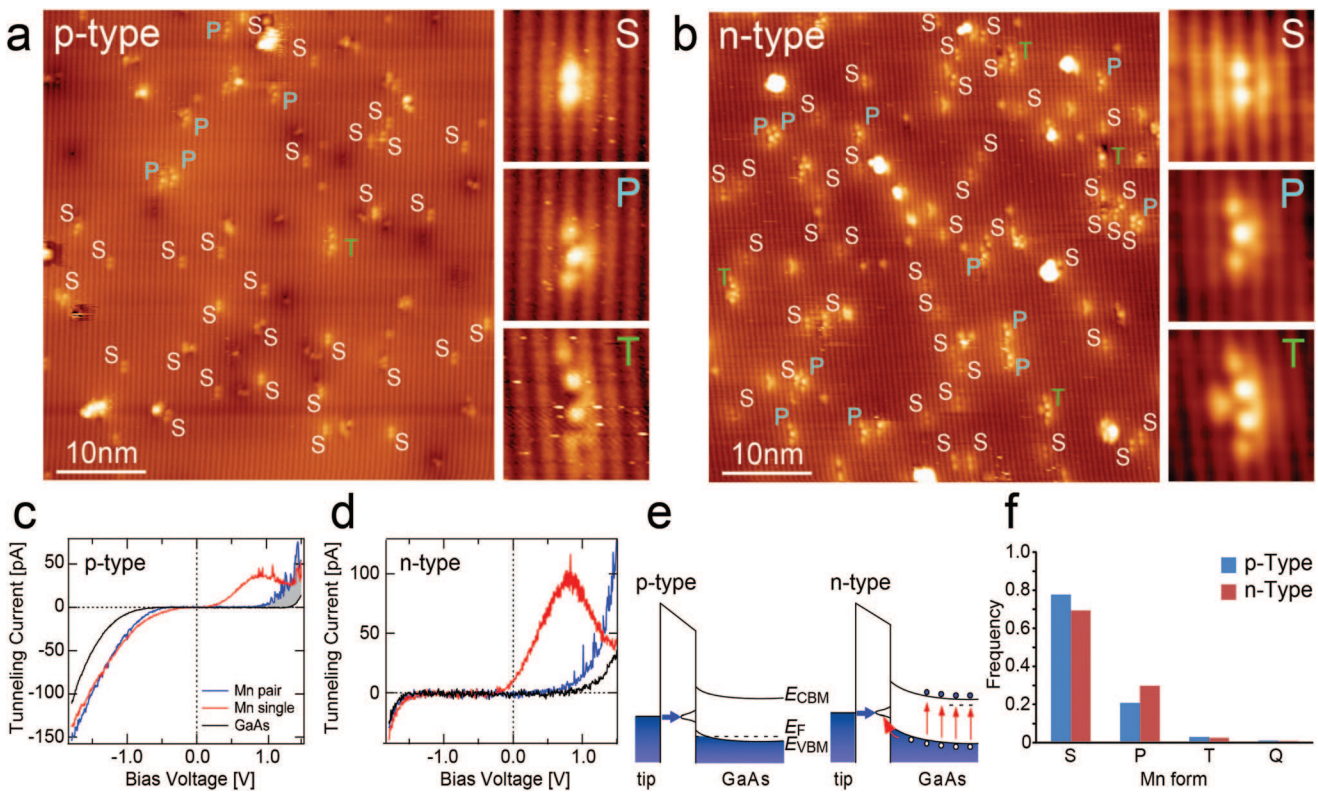

Fig. 1 Filled state STM images of Mn atoms deposited on (a) p-type (Zn-doped, 1 – 5 × 10^{17} cm^{-3}, V_S = −1.5 V, I_t = 0.05 nA) and (b) n-type (Si-doped, 1–5 × 10^{17} cm^{-3}, V_S = −1.5 V, I_t = 0.05 nA) GaAs(110) surfaces at room temperature. Single, pair, and trimer Mn images are labelled S, P, and T, and their magnified images are shown on the right side of the wide-scan images. (c), (d) Spectra obtained above a bare GaAs (black) and the structures of S (red) and P (blue) for p-type and n-type samples. The origin of the signal which appeared in Fig. 2 (f) is shown in (c). (e) Schematic illustrations of the band structures with Mn atoms. Sample was illuminated in the case of n-type to reduce the tip-induced band bending induced for positive sample bias voltages (635 nm, 0.5 mW), which was necessary to observe the acceptor level. (f) Histogram of ratio among structures labelled S, P and T in (a) and (b).

Fig. 2(a) – (e) show an example of the direct observation of the structural changes of a Mn pair during STS measurement for a p-type sample. Schematic illustrations of their structural models are shown together, where P^2_{110}(Ga), for example, indicates the pair structure with two Mn atoms located in the second-nearest-neighbouring sites in the <110> direction with a Ga atom, as shown in the schematic illustrations. STM tip scanning was carried out from left to right and bottom to top. Fig. 2(f) and (g) show the current maps deduced from I–V curves for V_s = +1.35 V and +0.8 V, respectively, which are considered to be related to the electronic structures of pair and single Mn structures, respectively. Since I–V curves were noisy owing to the structural change during STS measurement, integrated current images are shown here instead of differential images. As expected from the I–V curve shown in Fig. 1(c), no signal related to S (V_s = +0.8 V) was observed, whereas a spatial distribution of the electronic structure related to P (V_s = +1.35 V), which is shown in Fig. 1(c), was observed. During the next scan, P^2_{110}(Ga) changed into P^2_{110}, as shown in Fig. 2(b). Fig. 2(c) shows the STM image of P^2_{110}, which was obtained without spectroscopy because P^2_{110} was very unstable. In fact, when the next scan was started, it easily changed into P^1_{110} shown in Fig. 2(d). Therefore, a clear current map over the total structure could not be obtained for P^2_{110}. A partially obtained current map obtained for the structure shown in Fig. 2(b) is shown in Fig. 2(h). Subsequent changes are shown in Fig. 2(d) and (e). Fig. 2(i) and (j) show the current maps obtained for P^1_{110} and P_{111} shown in Fig. 2(d) and (e), respectively.

The electronic structure at V_s = +0.8 V was located above the Mn site for S, as shown in Fig. 2(k) and (l), whereas it was located between two Mn atoms for pair structures. The I–V curves averaged over the squares drawn in Fig. 2(h)–(j) and (l) are shown in Fig. 2(m). The difference between the spectra of S and P^1_{110} is clear and the spectral characteristics obtained for P_{111} and P^2_{110} are between those for S and P^1_{110}, showing a change in the degree of attractive interaction between Mn atoms. Spatial distributions for the structures of 2(b) to (e) for V_s = +1.35 V (not shown) were not clearly discriminated from those for V_s = +0.8 V, possibly because of the fact that the integrated signals are used here and they are not sensitive to the spectral changes shown in Fig. 2(m).

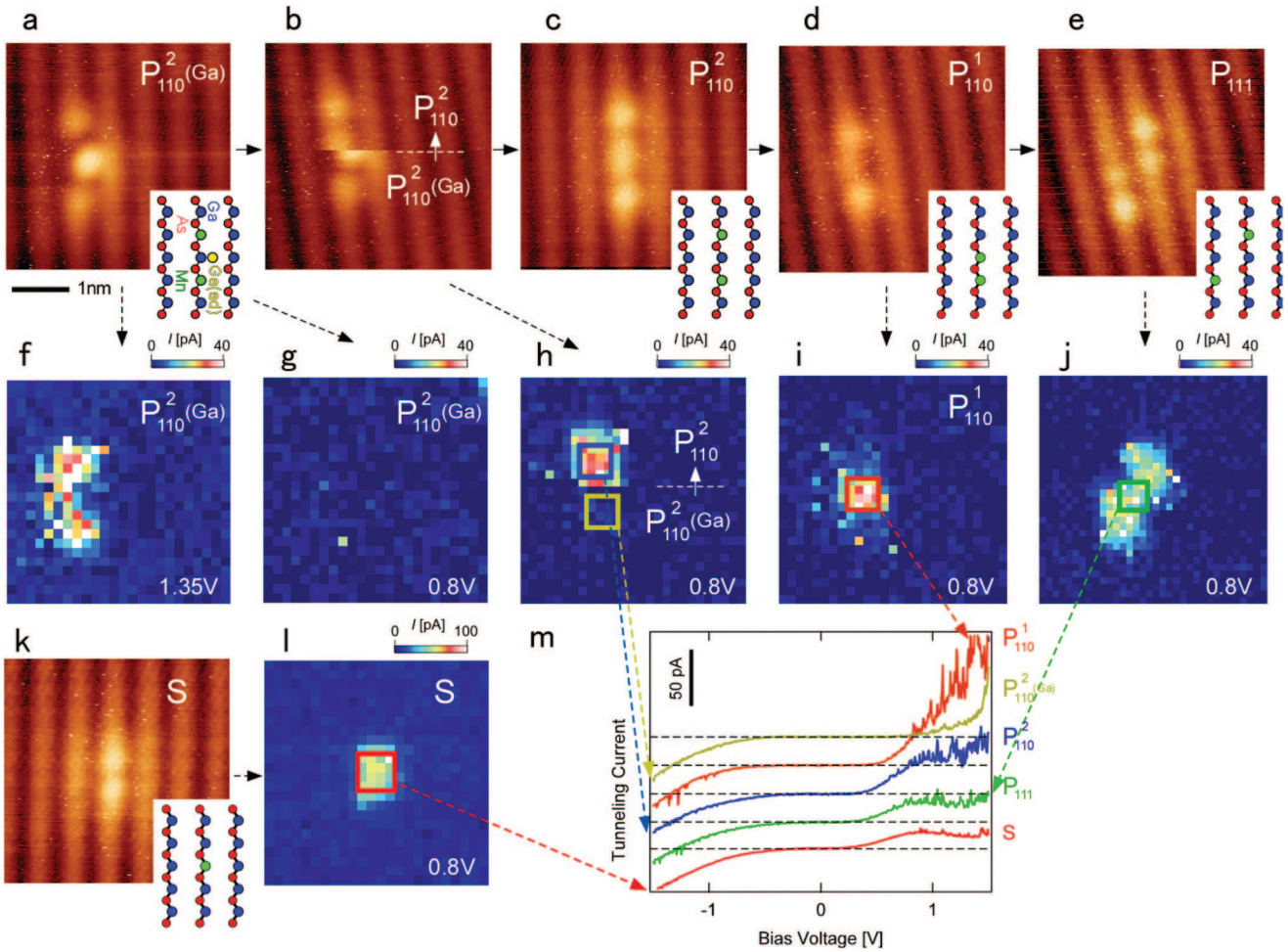

Fig. 2 (a)– (e) STM images of structural changes observed during STS measurement for the p-type sample. (f) and (g) Current images obtained for V_s = +1.35 V and V_s = +0.8 V. (h) to (j) Current images at V_s = +0.8 V obtained for structures shown in (b), (d), and (e), respectively. (k) and (l) STM image and its current map at V_s = +0.8 V obtained for the structure of single Mn labelled S in Fig. 1. (m) I– V curves averaged in squares drawn in (h) to (j) and (l).

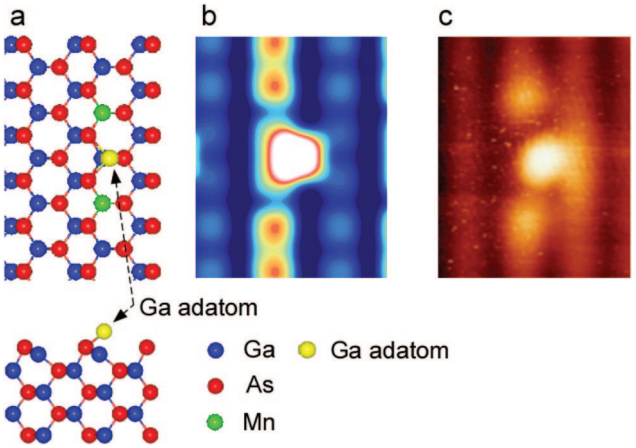

Fig. 3 Schematic illustrations (a) and simulated STM image (b) obtained for the structure of an Mn pair with a Ga atom shown in the schematic illustration (V_S = −1.0 V). Here, the Ga atom was placed at the brightest point in the STM image with a distance of 0.24 nm from the nearest neighbouring Ga atom below. (c) STM image for comparison (V_S = −1.5 V).

Although the STM image and spectrum obtained for the single Mn structure are similar to those obtained for the structure formed by atom manipulation at 4 K in the previous work, those obtained for the structure labelled P are different from the results obtained for any of the pair structures formed in the previous work,[10,11] namely, the structure P is asymmetric with respect to the <110> axis. However, since the structure P was transformed into a symmetric structure, one of the structures artificially formed at 4 K during STS measurement as is shown in Fig. 2, it is considered to be an intermediate structure naturally formed at RT.

Fig. 3 shows the STM images simulated for the structural model schematically shown for the structures labelled P observed in Fig. 1, where, as a possible structure, an additional Ga atom was placed as shown in the schematic model. We carried out a calculation based on a simple density functional theory (DFT) by constructing supercells with a slab model consisting offi ve GaAs(110) atomic layers and a vacuum region also with a thickness offi ve atomic layers.[15,16] The atoms in the topmost layer were displaced from the positions of the ideal GaAs(110) surface following the surface reconstruction.[17] The plane-wave cut-offenergy for the calculation was 50Ry.We used 2×2×1 Monkhorst – Pack k-point grids to sample the Brillouin zone. The Ga adatom is the most bright and the topmost As atoms in the neighbouring site of the Mn atom are brighter than the other As atoms.

Although a more detailed calculation is necessary to accurately determine the structure, the simulated image is in good agreement with the STM image, suggesting this to be an intermediate structure between the original one and that of the Mn pair without a Ga adatom artificially formed at 4 K. [18]

Similar structural and spectral changes during STS measurement were also observed for the Mn atoms deposited on an n-type substrate. An example of such observations is shown in Fig. 4. Single Mn structures were stable and used as a marker to show the changes in the pair structures. The yellow triangles in 4(a), (e) and (g) indicate the change in the position of the Mn pair. The observed results for the re-pairing of unpaired Mn atoms for both the p- and n-type samples are considered to support the existence of an attractive interaction between Mn atoms on the GaAs(110) surface. Pairing of Mn was not observed for a p-type sample when Mn atoms were deposited at 4 K, however, its appearance at RT suggests a rather low barrier height for the replacement of Ga by Mn. In either case, the arrangement of Mn atoms in a pair structure naturally formed at RT was in the <110> direction, which is required to realize a high-T_c (Ga, Mn)As.

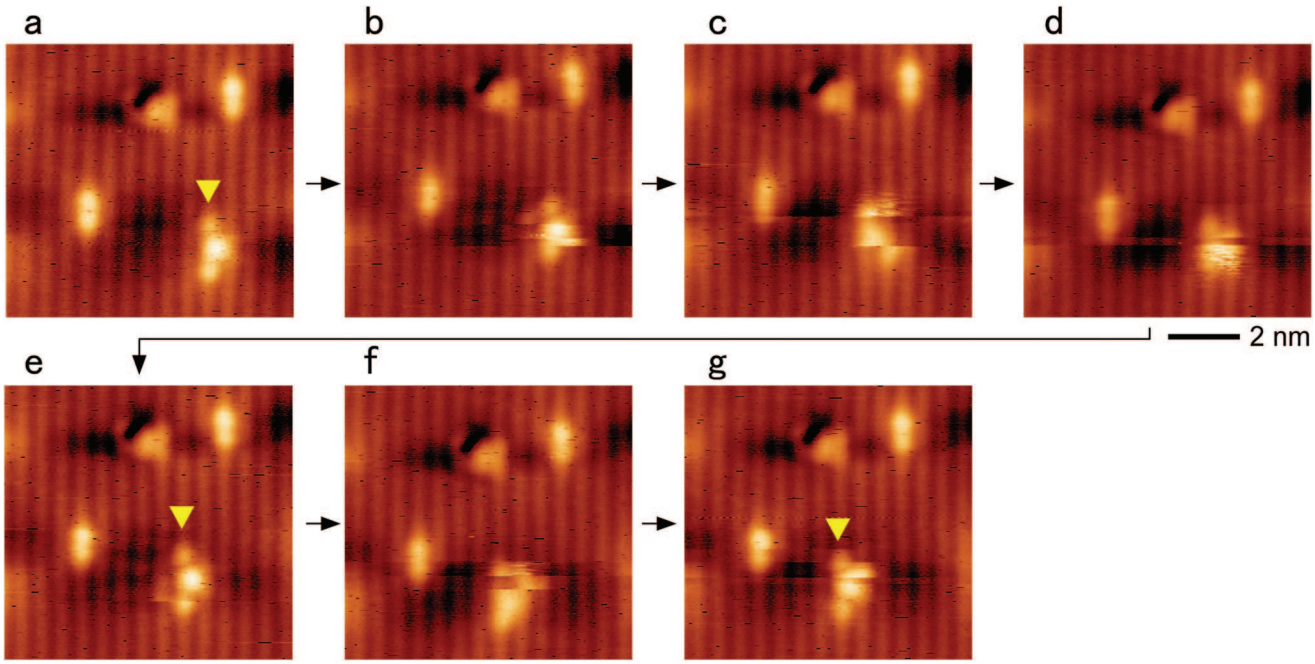

Fig. 4 STM images of structural changes observed during STS measurement for the n-type sample. The yellow triangles indicate the positional change of the Mn pair during STS measurement.

Conclusions

Mn atoms deposited on a GaAs(110) surface at room temperature were paired with a probability higher than the random distribution. Re-pairing of unpaired Mn atoms was observed during STS measurement, with the change in I–V characteristics, showing the interaction between the paired Mn atoms. Mn atoms naturally formed in a pair and a trimer were aligned in the <110> direction, which was theoretically predicted to produce a high Curie temperature. With further optimization of the growth conditions, we may be able to realize a structure of Mn atoms aligned in the <110> direction, which will provide (Ga, Mn)As with a high T_c. Studies on the coverage dependent evolution of pair or trimer formations and how the configurations change with thermal annealing, which is left for future work, are expected to advance further understanding of the mechanism, which is under consideration.

Acknowledgements

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References

1 T. Dietl, Nat. Mater., 2010, 9, 965–974.
2 T. Dietl and H. Ohno, Rev. Mod. Phys. , 2014, 86.
3 S. Kuroda, N. Nishizawa, K. Takita, M. Mitome, Y. Bando, K. Osuch and T. Dietl, Nat. Mater., 2007, 6, 440–446.
4 T. Jungwirth, J. Wunderlich, V. Novak, K. Olejnik, B. L. Gallagher, R. P. Campion, K. W. Edmonds, A. W. Rushforth, A. J. Ferguson and P. Nemec, Rev. Mod. Phys., 2014, 86, 855–896.
5 H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno and K. Ohtani, Nature, 2000, 408, 944–946.
6 L. Chen, S. Yan, P. F. Xu, J. Lu, W. Z. Wang, J. J. Deng, X. Qian, Y. Ji and J. H. Zhao, Appl. Phys. Lett. , 2009, 95, 182505.
7 L. Chen, X. Yang, F. H. Yang, J. H. Zhao, J. Misuraca, P. Xiong and S. von Molnar, Nano Lett, 2011, 11, 2584 – 2589.
8 H. Katayama-Yoshida, K. Sato, T. Fukushima, M. Toyoda, H. Kizaki, V. A. Dinh and P. H. Dederichs, Phys. Status Solidi A , 2007, 204, 15–32.
9 M. Hirayama, A. Natori and J. Nakamura, Phys. Rev. B: Condens. Matter, 2013, 87.
10 D. Kitchen, A. Richardella, J. M. Tang, M. E. Flatte and A. Yazdani, Nature, 2006, 442, 436–439.
11 D. Kitchen, Dr. Thesis, University of Illinois, 2006.
12 K. Kanazawa, T. Nishimura, S. Yoshida, H. Shigekawa and S. Kuroda, Nanoscale , 2014, 6, 14667–14673.
13 P. Mahadevan, A. Zunger and D. D. Sarma, Phys. Rev. Lett. 2004, 93.
14 S. Yoshida, M. Yokota, O. Takeuchi, H. Oigawa, Y. Mera and H. Shigekawa, Appl. Phys. Express , 2013, 6.
15 X. Gonze, J. M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G. M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty and D. C. Allan, Comput. Mater. Sci, 2002, 25, 478–492.
16 X. Gonze, G. M. Rignanese, M. Verstraete, J. M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, P. Ghosez, M. Veithen, J. Y. Raty, V. Olevano, F. Bruneval, L. Reining, R. Godby, G. Onida, D. R. Hamann and D. C. Allan, Z. Kristallogr., 2005, 220, 558–562.
17 R. J. Meyer, C. B. Duke, A. Paton, A. Kahn, E. So, J. L. Yeh and P. Mark, Phys. Rev. B: Condens. Matter , 1979, 19, 5194 – 5205.
18 J. Tersoff and D. R. Hamann, Phys. Rev. Lett., 1983, 50, 1998–2001.