Room-temperature thousandfold magnetoresistance change in MnSb granular films: Magnetoresistive switch effect

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(Received 31 August 1999; accepted for publication 22 November 1999)

A huge positive magnetoresistance effect has been discovered in MnSb granular films. Granular film consisting of nanoscale MnSb dots that are grown on a sulfur-passivated GaAs (001) substrate by molecular-beam epitaxy, then covered with an Sb thin layer, exhibits magnetic-field-sensitive current–voltage characteristics. When a constant voltage, above the threshold value, is applied to the film, more than 1000% change in the current, which we term *magnetoresistive switch*, is driven by the magnetoresistance effect under a relatively low magnetic field (less than 0.5 T) at room temperature. © *2000 American Institute of Physics.* [S0003-6951(00)04303-5]

Magnetoresistance (MR) effect has been intensively studied in recent years with a view to its application in various electronic devices. Positive MR effect of a two-dimensional electron gas with high mobility observed in III–V based semiconductor heterostructures has been investigated for magnetic sensors in automotive technology.[1] In particular, the discovery of the giant (negative) MR effect caused by a spin-dependent scattering in metallic multilayers has stimulated a lot of interest in the underlying physics, as well as in applications such as magnetic data storage devices.[2,3] Since the giant MR effect depends on the combination of component materials, similar effects have been found in other structures, such as granular films[4–7] and tunneling junctions.[8]

In addition, MR effects intrinsic to a material, which should be distinguished from the above-mentioned MR effects, have been widely investigated. Examples include the so-called colossal MR of nonstoichiometric EuO[9] and mixed-valence manganese perovskites.[10] Research on colossal MR has been quite active in the manganites,[11] because these materials show an even larger MR effect (more than a thousandfold change) than the above-mentioned giant MR effect (100% at most). Recently, the research field of hybrid ferromagnet-semiconductor structures has emerged.[12–17] A large negative MR, three orders of magnitude, was reported in ErAs:GaAs nanocomposites.[18] The intrinsic MR effects and the extrinsic MR effects in the hybrid structures, however, only occur under large magnetic fields and/or low temperatures.

Here, we report a material showing more than 1000% positive MR effect under a low magnetic field, even at room temperature. The magnetoresistive switch effect driven by the huge MR effect is observed in manganese antimonide, MnSb, granular films. MnSb is a metal of the NiAs-type crystal structure and shows ferromagnetic transition at around 600 K.[19] MnSb dots were fabricated on sulfur-passivated semi-insulating ($>1\times10^7$ Ω cm) GaAs (001) substrates by molecular-beam epitaxy (MBE). The surface termination by group-VI elements, by sulfur in the present study, is one of the well-known techniques to fabricate dot structures on the GaAs substrate.[20] The deposited MnSb forms planoconvex dots on the substrate as shown in Fig. 1. The typical diameter and the height of a dot are 20 and 3–5 nm, respectively. The MnSb dots were covered with an Sb thin layer in the MBE chamber. The growth procedure will be reported in detail elsewhere.[21] In this letter, the discussion will focus on the MR effects of MnSb granular films. MR properties of granular film with the nominal MnSb thickness of 0.2 nm are introduced.[22] After unloading the granular film from the MBE chamber, transport measurements of the film were performed at room temperature in air. The electric contacts were made by indium solder or gold paste. Magnetization measurements indicated that the granular film including MnSb dots was superparamagnetic at room temperature.

The current–voltage (I–V) characteristics of the films were measured by a two-probe method. The voltage was swept quasistatically.[23] The magnetic field up to 1.5 T was applied parallel to the film plane. The I–V curves are nonlinear (nonohmic), and the curve is abruptly switched from the low-current (high-resistance) state to the high-current (low-resistance) state at 52 V in the increase-voltage scan under zero magnetic field, as shown in Fig. 2(a). The transition shows the hysteretic behavior in the decreasing-voltage scan. When the magnetic field of 1.5 T is applied to the film, the transition driven by the applied voltage disappears. The figure shows that the switch of two resistive states can be achieved not only by an electric field (voltage), but also by a magnetic field. Since the current change above the threshold voltage is extremely large, the observed decrease of the current (the increase of the resistance) by the magnetic field (i.e., the positive MR effect), which we term the magnetoresistive switch effect, is drastic. For example, the switch ratio at the constant voltage of 80 V, defined in this report as $\Delta I/I(H)=(I(0)-I(H))/I(H)$, reaches about 3500% ($H=1.5$ T).

The present huge magnetoresistive switch effect is extremely sensitive to the nominal thickness of MnSb and the

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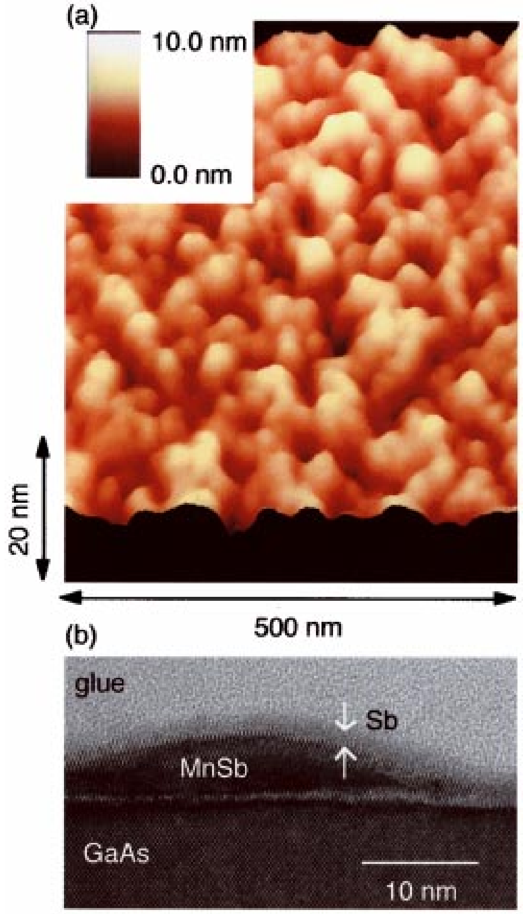

FIG. 1. (Color) Nanoscale MnSb dots grown on a sulfur-passivated GaAs (001) substrate, then covered by a Sb cap layer of 3 nm. The nominal MnSb thickness of the granular film is 0.2 nm. (a) Typical atomic force microscopy image of the MnSb granular film. (b) Typical high-resolution cross-sectional transmission electron microscopy (TEM) image of the MnSb granular film.

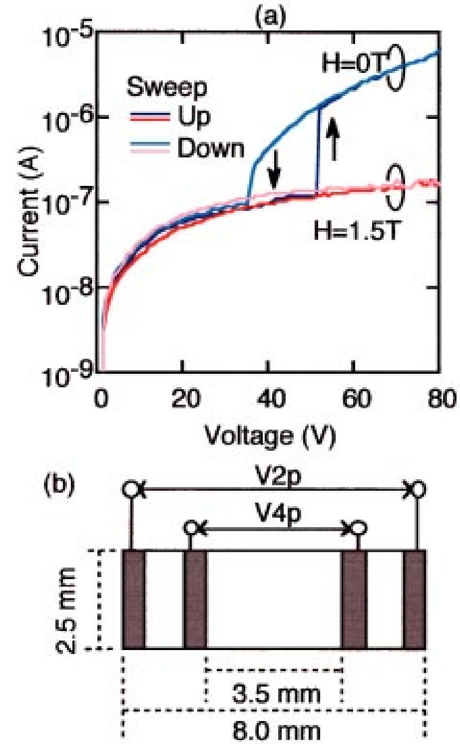

FIG. 2. (Color) (a) Current–voltage (I–V) characteristics of the MnSb granular film with the nominal MnSb thickness of 0.2 nm. The I–V curves were measured at room temperature by a two-probe method. The curves measured under 0 and 1.5 T are indicated by blue and red lines. The sweep directions of up and down represent the increase and the decrease of the voltage, and they are shown by deep and light colors, respectively. The arrows beside the hysteresis indicate the scan direction. (b) The sample of the MnSb granular film which was used for transport measurements. The emerged voltages in two- and four-probe configurations are referred to in this letter as $V2p$ and $V4p$, respectively.

topological features of the granular film, such as the size of MnSb dots. We grew the granular films with the nominal MnSb thicknesses from 0 to 1.4 nm. The magnetoresistive switch effect was, however, observed only in the thickness range between 0.2 and 0.7 nm. In this range, no distinct change in the size of MnSb dots was observed, but the density of the dots increased with the increase of the nominal MnSb thickness.[21] When the nominal MnSb thickness was more than 1 nm, the granular films showed lower resistance with no anomalous I–V behavior, but anisotropic MR effect (a few % at most) was observed. Furthermore, even when the nominal MnSb thickness is 0.7 nm, the switch effect did not appear in the case where the average size of the dots is larger, for example two times larger, than that of the present film. These facts indicate that the existence of MnSb dots with the peculiar topological conduction plays a crucial role in the magnetoresistive switch effect. In the present film, when the voltage was applied in the opposite direction, the I–V curve was also nonlinear, but the switch ratio was smaller (about 30%) and the hysteretic behavior did not appear up to 80 V. The reason for the asymmetric behavior is thought to be due to the imhomogeneity of the granular film, but this has not yet been fully investigated.

To further clarify the phenomenological characteristics of the magnetoresistive switch effect, the magnetic field dependence of the resistance and the current of the MnSb granular film were measured. The sweep rate of the magnetic field was kept at about 0.2 T/min for all measurements presented in Fig. 3. The measurement was carried out by applying a constant voltage, *V2p*, indicated in each figure. As shown in Fig. 3(a), when the constant voltage of 68 V is applied, the two-probe resistance, $V2p/I$, rises by more than one order of magnitude from the low-resistance state. The resistance-increase finishes at around 0.5 T. The resistance explosion is also observed in the four-probe resistance, $V4p/I$ [Fig. 3(b)]. The MR ratio of the four-probe resistance is smaller than that of the two-probe resistance, but still more than 200%. This fact shows that the magnetoresistive switch effect is the intrinsic property of the MnSb granular film. The enhancement of the MR ratio in the two-probe configuration may indicate that the voltage drop mainly takes place near the electric contacts. Generally, the MR behavior of granular materials is described by the square of the magnetization.[5] The curvature of the magnetic field dependence of the current is well expressed by the relationship [Fig. 3(c)]. Therefore, it is reasonable to consider that the switch effect arises from the existence of MnSb dots in the granular film. The driving force of the switch operation seems to be coupled strongly with the magnetization reversal of MnSb dots. The magnetoresistive switch effect becomes more magnetic-field sensitive, when the constant voltage is set at the hysteretic region, as is seen in Fig. 3(d). The resistance rise by the

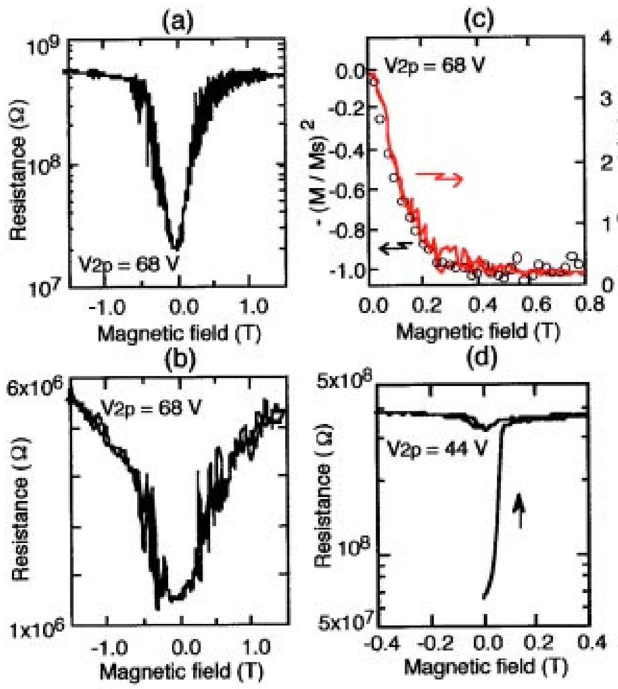

FIG. 3. (Color) The magnetoresistive switch effect observed at room temperature in the MnSb granular film with the nominal MnSb thickness of 0.2 nm. Magnetic fields were applied parallel to the film plane. The sweep direction of the magnetic field was first from zero to plus 1.5 T, second from plus 1.5 T to minus 1.5 T, and last from minus 1.5 T to zero. The sweep rate was kept at about 0.2 T/min. (a) The magnetic field dependence of the two-probe resistance, $V2p/I$. $\Delta R/R(0)=[R(1.5T)-R(0)]/R(0) \approx 2400\%$, $\Delta R/R(1.5T)\approx 96\%$. (b) The magnetic field dependence of the four-probe resistance, $V4p/I$. $\Delta R/R(0)\approx 260\%$. The four-probe measurement was carried out by applying the constant voltage of 68 V. (c) The comparison of the magnetic field dependence of the current (red lines) with the curvature of the square magnetization normalized by the saturation magnetization, *Ms*, (open circles). (d) Irreversible two-probe magnetoresistance change observed when the constant voltage was settled in the hysteretic region of the *I–V* curve. The arrow indicates the sweep direction of the magnetic field.

applied magnetic field is much faster than the magnetization evolution. The transition is almost completed at 0.08 T. The noisy behavior, observed in MR curves of Fig. 3(a), indicating temporal fluctuations between high and low resistance states, disappears in the MR curve observed in the hysteretic region. Since this switch effect is not revertible, the MnSb granular film may have some potential for the application to devices with memory functions.

Two important questions remain to be considered, the physical origin of the switch effect and the segment where the switch operation occurs. Several spin-dependent transport models have been constructed to understand the negative MR in various granular materials.[3–6,14,18] However, no established model can relate the positive MR of the magnetoresistive switch effect. The observed *I–V* curve reminds us of a junction showing an electric breakdown above a threshold voltage. Given that the applied magnetic field restores the junction from the breakdown, one possibility is to assume that this behavior is due to a Coulomb blockade effect where the spin-dependent Coulomb gap is enlarged by a magnetization alignment of MnSb dots. The underlying physics of the restoration is still under investigation. Although bulk Sb is (semi-) metallic, the resistance of the Sb cap layer, namely the granular film with zero nominal thickness of MnSb, was very high. The assignment of the switching segment has not yet been successfully done, but the origin of junctions may be attributable to the Sb thin cap layer. The contribution of the interface between MnSb dots and the sulfur-passivated GaAs to the transport property needs further investigation. Nevertheless, the MnSb granular film showing the magnetoresistive switching effect affords great promise in terms of applications. First, the fabrication of this material is fully compatible with the fabrication of semiconductor-based devices. Second, since the magnetic-field sensitivity of the switch effect is not limited by the intrinsic material properties of MnSb, the sensitivity can be further improved.

This work was performed at JRCAT under the joint research agreement between NAIR and the Angstrom Technology Partnership (ATP). This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) and partially by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

[1] J. Heremans, D. L. Partin, D. T. Morelli, B. K. Fuller, and C. M. Thrush, Appl. Phys. Lett. **57**, 291 (1990).
[2] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
[3] W. J. Gallagher, S. S. P. Parkin, Y. Lu, X. P. Bian, A. Marley, K. P. Roche, R. A. Altman, S. A. Rishton, C. Jahnes, T. M. Shaw, and G. Xiao, J. Appl. Phys. **81**, 3741 (1997).
[4] A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992).
[5] J. Q. Xiao, J. Jiang, and C. L. Chien, Phys. Rev. Lett. **68**, 3749 (1992).
[6] J. M. D. Coey, A. E. Berkowitz, Li. Balcells, F. F. Putris, and A. Barry, Phys. Rev. Lett. **80**, 3815 (1998).
[7] S. M. Jordan, R. Schad, A. M. Keen, M. Bischoff, D. S. Schmool, and H. van Kempen, Phys. Rev. B **59**, 7350 (1999).
[8] T. Miyazaki and N. Tezuka, J. Magn. Magn. Mater. **139**, L231 (1995).
[9] T. Penney, M. W. Schafer, and J. B. Torrance, Phys. Rev. B **5**, 3669 (1972).
[10] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[11] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature (London) **388**, 50 (1997).
[12] G. A. Prinz, Science **250**, 1092 (1990).
[13] J. Shi, J. M. Kikkawa, R. Protsch, T. Schäffer, D. D. Awschalom, G. Medeiros-Ribeiro, and P. M. Petroff, Nature (London) **377**, 707 (1995).
[14] H. Akinaga, J. De Boeck, G. Borghs, S. Miyanishi, A. Asamitsu, W. Van Roy, Y. Tomioka, and L. H. Kuo, Appl. Phys. Lett. **72**, 3368 (1998).
[15] K. Ando, A. Chiba, and H. Tanoue, Appl. Phys. Lett. **73**, 387 (1998).
[16] P. J. Wellmann, J. M. Garcia, J.-L. Feng, and P. M. Petroff, Appl. Phys. Lett. **73**, 3291 (1998).
[17] H. Ohno, Science **281**, 951 (1998).
[18] D. R. Schmidt, A. G. Petukhov, F. Foygel, J. P. Ibbetson, and S. J. Allen, Phys. Rev. Lett. **82**, 823 (1999).
[19] K. Adachi and S. Ogawa, *Landolt-Bornstein New Series III/27a*, edited by H. P. J. Wijn (Springer, Berlin, 1988), p. 148.
[20] Y. Watanabe, T. Scimeca, F. Maeda, and M. Oshima, Jpn. J. Appl. Phys., Part 1 **33**, 698 (1994).
[21] M. Mizuguchi, H. Akinaga, K. Ono, and M. Oshima (unpublished).
[22] The nominal thickness of MnSb means the thickness, *d*, in the case that the deposited atoms form the uniform MnSb thin film on the substrate. *d* is decided as $T_{\mathrm{depo}}\times 100\ [\mathrm{nm}]/T_{100}$, where T_{depo} and T_{100} are the deposition times of MnSb dots and a uniform MnSb film with the thickness of 100 nm, respectively.
[23] A staircase-like voltage scan was performed. After the increase or decrease of voltage (1 V step), the voltage was kept at a constant value for 10 sec, then the current was measured.