Transactions of the Materials Research Society of Japan 25 [4] 1119-1122 (2000)

Enormous Magnetoresistance Effect in Hybrid Ferromagnetic-Nanocluster / Semiconductor Films

Hiroyuki Akinaga, Masaki Mizuguchi, Kanta Ono* and Masaharu Oshima*
Joint Research Center for Atom Technology (JRCAT) : National Institute for Advanced Interdisciplinary Research (NAIR), 1-1-4 Higashi, Tsukuba, Ibaraki 305-8562, Japan
FAX : 81-298-54-2777, e-mail : akinaga@jrcat.or.jp
* Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
FAX : 81-3-5841-8744, e-mail : oshima@sr.t.u-tokyo.ac.jp

We have discovered a huge positive magnetoresistance effect, more than 1000 % at room temperature (RT), in novel hybrid ferromagnet / semiconductor granular films. The granular film consists of ferromagnetic MnSb nanoclusters (the typical diameter and the height of a cluster are 20 and 3 ~ 5 nm, respectively) grown on a sulfur passivated (001) GaAs substrate by molecular beam epitaxy, and then covered with an Sb thin layer. The film shows magnetic-field sensitive current-voltage characteristics. When a constant voltage, above the threshold value, is applied to the granular film, very steep change in the current, which we term "magnetoresistive switch effect", is induced by the magnetoresistance effect under a relatively low magnetic field. Similarities between the magnetoresistive switch effect and Ovshinsky switch effect are discussed.
Key words : magnetoresistance effect, nanocluster, magnetoresistive switch effect, MnSb, GaAs

1. INTRODUCTION

Recently, the new research field of hybrid ferromagnet-semiconductor structures has emerged. Based on the results of the fabrication of high-quality ferromagnetic epitaxial films on semiconductor substrates, more advanced hybrid structure, such as a multilayer of ferromagnetic metals and semiconductors, has been studied.[1,2] The other interesting class of the hybrid system is a ferromagnetic metal cluster combined with a semiconductor.[3] Large magneto-optical effect was observed in GaAs with magnetic MnAs nanoclusters.[4] The tunneling magnetoresistance (MR) between ferromagnetic MnAs clusters through GaAs was reported.[5] The ErAs-based granular films with ten layers of ErAs nanoscale islands separated by GaAs spacer layer exhibited the negative MR (4 orders of magnitude at 1.6 K in 3 T).[6] On the other hand, the research on mixed-valence manganese perovskites has become quite active very recently.[7] This is because these materials also show the larger MR effect (more than a thousand-fold change) than the MR effect (one hundred percent at most) of metallic magnetic materials which have been already adopted in applications such as magnetic data storage devices.[8] However, the above-mentioned MR phenomena of hybrid systems and manganites require low temperatures and / or high magnetic fields.[9]

In this report, we show a material showing more than 1000 % positive MR effect under a low magnetic field, even at room temperature (RT). The magnetoresistive switch effect driven by the huge MR effect is observed in manganese antimonide, MnSb, granular films grown on sulfur passivated GaAs substrates.

2. SAMPLE PREPARATION

MnSb is a metal of the NiAs-type crystal structure and shows ferromagnetic transition at around 600 K. MnSb clusters were fabricated on sulfur-passivated semi-insulating (> 1×10^7 Ωcm) GaAs (001) substrates by molecular-beam epitaxy (MBE). To terminate the surface by sulfur, the substrate was dipped into an $(NH_4)S_x$ solution for 1 hour. 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.[10] After the termination and being degassed in a loading chamber, the thermal cleaning of the substrate was performed at 400 ~ 500 °C in ultra high vacuum. The flux ratio of Sb / Mn was set at 4 ~ 5, and the growth rate of MnSb was estimated to be 1 nm / min. The growth procedure will be described in detail elsewhere.[11] In this letter, the discussion will be focused on the MR effects of MnSb granular films with the nominal MnSb thickness of 0.2 nm.[12] The deposited MnSb forms plano-convex clusters on the substrate as shown in Fig. 1. The typical diameter and the height of a cluster are 20 and 3 - 5 nm, respectively. The MnSb clusters were covered with an Sb thin layer at around RT in the MBE chamber.

3. MAGNETOTRANSPORT MEASUREMENTS

After unloading the granular film from the MBE chamber, transport measurements of the film were performed at RT in air. The electric contacts were

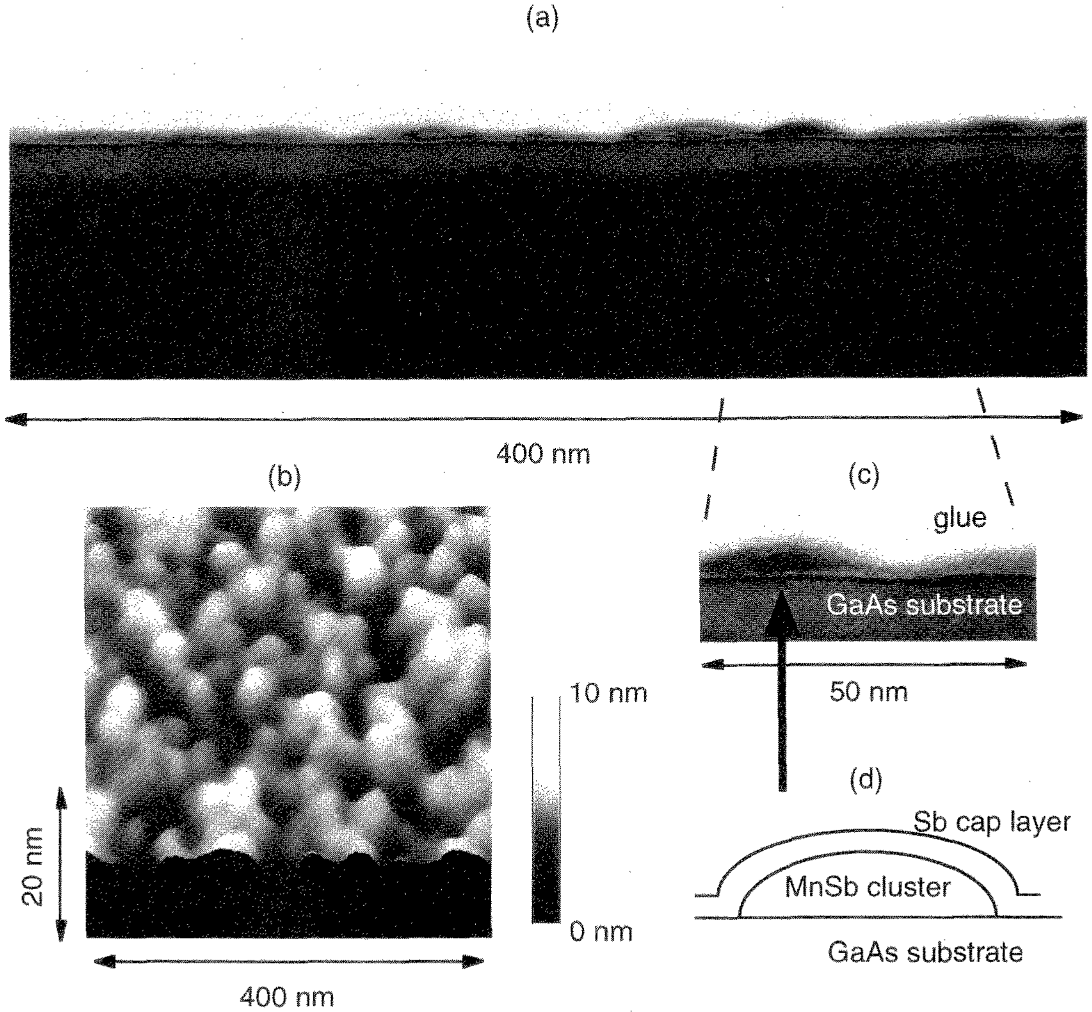

Fig.1 Nanoscale MnSb dots grown on a sulfur passivated GaAs (001) substrate, then covered by a Sb cap layer of 3 nm. (a) Typical cross-sectional transmission electron microscopy (TEM) image of the MnSb granular film. (b) Typical atomic force microscopy image of the MnSb granular film. (c) The magnified cross-sectional TEM image of the MnSb cluster. (d) The schematic drawing of the MnSb cluster grown on the GaAs substrate.

made by indium solder. Since the change of the film-resistance as a function of the voltage and the magnetic field was quite huge, the current-voltage (*I-V*) characteristics and the MR curves of the films were measured by a 2-probe method. The schematic configuration of the measurement is shown in Fig.2(a). The magnetic field up to 1.5 T was applied parallel to the film plane for both measurements.

Fig. 2(b) shows the *I-V* curves of the Sb capped MnSb granular film. (Note : the current value is shown logarithmically.) The *I-V* curves were measured using a HP4156 precision semiconductor parameter analyzer. The sweep rate of the voltage was about 1.5 V / sec. The I-V curves are almost linear (Ohmic) up to 40 V. Then, the curve switched from the linear state to the superlinear state (non-Ohmic) under zero magnetic field. The small hysteretic behavior appears in the decreasing-voltage scan. When the magnetic field of 1.5 T is applied to the film, the superlinear part driven by the applied voltage disappears and becomes sublinear. The figure shows that the switch of two resistive states, namely the switch from superlinear to sublinear, 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 enormous. For example, the switch ratio at the constant voltage of 100 V, defined in this report as $\Delta I / I(\mathrm{H}) = (I(0) - I(\mathrm{H})) / I(\mathrm{H})$, reaches about 7500 % (H = 1.5 T).

To clarify the phenomenological characteristics of the magnetoresistive switch effect,

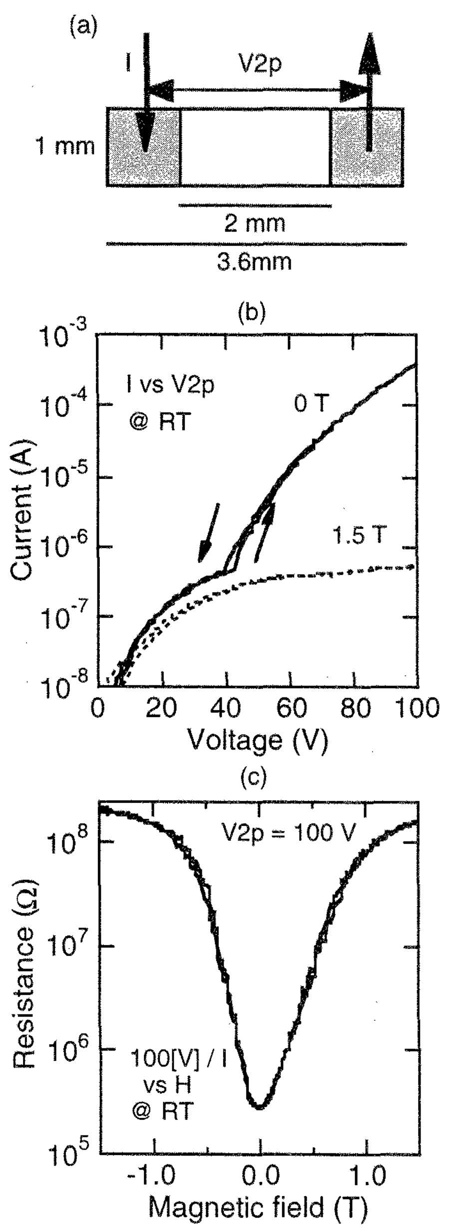

Fig.2 (a) The sample of the MnSb granular film which was used for transport measurements. The emerged voltage in the 2-probe configuration is referred to in this letter as *V2p*. (b) Current-voltage (*I-V*) characteristics at RT of the MnSb granular film with the nominal MnSb thickness of 0.2 nm. The curves measured under 0 and 1.5 T are indicated by solid and broken lines, respectively. The sweep directions are shown by up and down arrows. (c) The magnetoresistance curve at RT measured by applying the constant voltage of 100 V.

the magnetic field dependence of the resistance of the MnSb granular film was measured. The MR curves were measured by applying a constant voltage, *V2p*, using a conventional MR measurement set-up. As shown in Fig. 2(c), when the constant voltage of 100 V is applied, the 2-probe resistance, $V2p / I$, rises by more than 2 order of magnitude by applying magnetic field. The MR ratio defined in this report as $\Delta R / R(0T) = (R(1.5T) - R(0T)) / R(0T)$ becomes 7500 % (The other kind of MR ratio, $\Delta R / R(1.5T)$, which is occasionally used, is 99.9 %.).

4. DISCUSSION

We are confronted by two important questions, the physical origin of the switch effect and the segment where the switch operation occurs. Several spin-dependent transport models have been constructed to explain the negative MR in various granular materials.[13,14] However, no established model can give 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. This behavior is quite similar to that of the Ovshinsky switch effect which was observed in various types of disordered semiconducting materials.[15] TEM observations revealed that the Sb cap layer was polycrystalline. Although bulk Sb is (semi-) metallic, the resistance of the Sb cap layer, namely the granular film with zero nominal thickness of MnSb, was rather high. The Sb cap layer with MnSb clusters may plays the same role of the disordered material. One of the characteristics

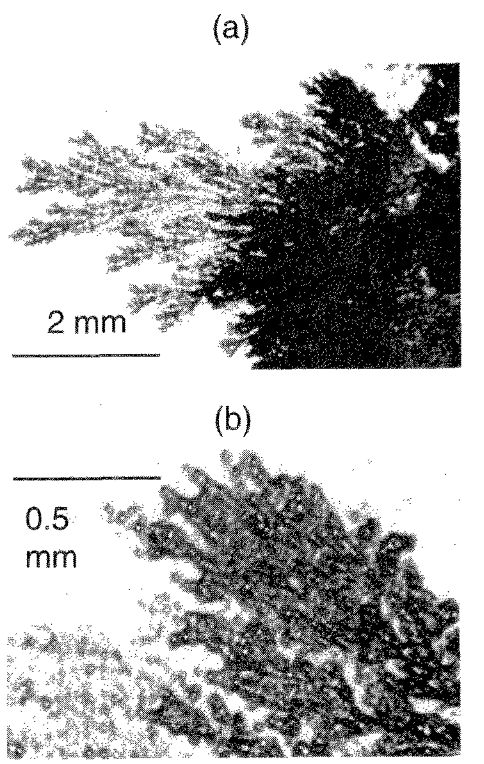

Fig.3 Optical microscope images of the filamentary-breakdown behavior of the MnSb granular film.

of the Ovshinsky effect is the filamentary conduction.[16] Fig. 3 shows the optical microscope image of the MnSb granular film after applying larger voltage than the threshold of the sample-destruction. The filamentary conductance cannot be proved directly, but it seems likely that the electric conduction in the granular film at the superlinear part shown in Fig. 2(b) occurs in the filamentary conductance path. The contribution of the interface between MnSb dots and the sulfur-passivated GaAs to the transport property also needs an investigation.

5. CONCLUSION

We showed the magnetoresistive switch effect, more than 1000 % positive MR effect at RT, in MnSb granular films grown on GaAs substrates. This is the largest MR effect at RT so far. Although the behavior has similarities to that of the Ovshinsky switch effect, the origin of the magnetoresistive switch effect has not yet been fully understood. Nevertheless, the MnSb granular film affords great promise in terms of magneto-electronics applications. The fabrication of this magnetic material is compatible with the fabrication of semiconductor-based devices.

ACKNOWLEDGEMENTS

This work was performed at JRCAT under the joint research agreement between NAIR and the Angstrom Technology Partnership (ATP), and JRCAT and Univ. Tokyo. 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.

REFERENCES

1. K. Inomata, K. Yasu and Y. Saito, *Phys. Rev. Lett.*, **74**, 1863-66 (1995).
2. W. Van Roy, H. Akinaga, S. Miyanishi and A. Asamitsu, *Appl. Phys. Lett.*, **71**, 971-73 (1997).
3. J. Shi, J. M. Kikkawa, R. Proksch, T. Schäffer, D. D. Awschalom, G. Medeiros-Ribeiro, and P. M. Petroff, *Nature*, **377**, 707-10 (1995).
4. H. Akinaga, S. Miyanishi, K. Tanaka, W. Van Roy and K. Onodera, *Appl. Phys. Lett.*, **76**, 97-99 (2000).
5. H. Akinaga, J. De Boeck, G. Borghs, S. Miyanishi, A. Asamitsu, W. Van Roy, Y. Tomioka and L.H. Kuo, *Appl. Phys. Lett.*, **72**, 3368-70 (1998).
6. D.R. Schmidt, A.G. Petukhov, F. Foygel, J.P. Ibbetson, S.J. Allen, *Phys. Rev. Lett.*, **82**, 823-26 (1999).
7. A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, *Nature*, **388**, 50-52 (1997).
8. W.J. Gallagher, S.S.P. Parkin, Yu Lu, X.P. Bian, A. Marley, K.P. Roche, R.A. Altman, S.A. Rishton, C. Jahnes, T.M. Shaw, and Gang Xiao, *J. Appl. Phys.*, **81**, 3741-46 (1997).
9. K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature*, **395**, 677-80 (1998).
10. Y. Watanabe, T. Scimeca, F. Maeda, M. Oshima, *Jpn. J. Appl. Phys.*, **33**, 698-701 (1994).
11. M. Mizuguchi, H. Akinaga, K. Ono and M. Oshima, to be published in *J. Cryst. Growth*.
12. The nominal thickness of MnSb means the thickness, d, in the case that the deposited atoms form the uniform MnSb thin film on the GaAs substrate. d is described as
    $d = T\text{depo} \times 100$ [nm] / $T100$,
    where Tdepo and $T100$ are the deposition times of MnSb dots and a uniform MnSb film with the thickness of 100 nm, respectively.
13. 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**, 3745-48 (1992).
14. John Q. Xiao, J. Samuel Jiang, and C.L. Chien, *Phys. Rev. Lett.*, **68**, 3749-52 (1992).
15. S.R. Ovshinsky, *Phys. Rev. Lett.*, **21**, 1450-53 (1968).
16. A.D. Pearson and C.E. Miller, *Appl. Phys. Lett.*, **14**, 280-282 (1969).

(Received December 16, 1999; Accepted May 6, 2000)