Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp1161-1162

Electronic Band Structure of TiN/MgO-4x4 and 5x5 nanostructures

Kazuaki Kobayashi[1], Hirokazu Takaki[1,3] , Masato Shimono[2], Nobuhiko Kobayashi[3], and Kenji Hirose[4]

[1] International Center for Materials Nanoarchitechtonics (MANA), National Institute for Materials Science
Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
Phone: +81-29-860-4511 E-mail: KOBAYASHI.Kazuaki@nims.go.jp
[2] Research Center for Structural Materials (RCSM), National Institute for Materials Science
Sengen 1-2-1, Tsukuba, Ibaraki, 305-0047, Japan
[3] Univ. of Tsukuba, Institute of Applied Physics, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan
[4] NEC Corporation, Smart Energy Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

Abstract

Nanostructured TiN(001)/MgO(001)-4x4 and 5x5 superlattices based on a repeated slab model have been investigated. Their electronic states of TiN dot/MgO(001)-4x4 and 5x5 superlattices are obtained by using the total energy pseudopotential method. All of them correspond to semiconductor. Their electronic properties depend on a shape of the TiN dot and a size of the MgO substrate.

1. Introduction

We have investigated TiN(001)/MgO(001)-1x1, 2x1, 2x2, and 3x3 superlattices previously [1-3] in order to support an experiment [4] of the TiN thin film on an MgO substrate using molecular beam epitaxy. We present TiN(001) dot/MgO(001) as TiN dot/MgO hereafter. TiN dot structures (rectangular and rectangular parallelepiped) will be mentioned in the next section. The electronic structures of the rectangular TiN dot/MgO-2x2 and 3x3 superlattices are semiconducting [3]. Other TiN/MgO superlattices correspond to metallicity [1-3]. Nanostructured materials are focused on enhancing the thermoelectric properties [5-8]. Therefore, we have calculated thermoelectric properties (Seebeck coefficients, thermal conductance, and figure of merit [*ZT*]) of TiN/MgO-1x1 and 2x2 superlattices using Non-equilibrium Green Function (NEGF) method [9-11].

In this study, the TiN dot structures on MgO-4x4 and 5x5 substrates are considered as shown in Fig. 1. The main purpose of this study is to obtain structurally relaxed TiN dot/MgO superlattices. Another important purpose is to obtain their electronic properties as nanostructured TiN dot/MgO superlattices. A nonmetallic state is more suitable to enhance thermoelectric properties than a metallic state. It is expected that small TiN dot structures on the large MgO substrates as 4x4 and 5x5 will be nonmetallic and larger band gap values.

2. Method of Calculations

The present calculation is based on local density approximation (LDA) in density functional theory (DFT) [12,13] with the Wigner [14] formula for the exchange-correlation. The optimized pseudopotentials [15,16] are used for Ti, Mg, N, and O, and their nonlocal parts are transformed to the Kleinman-Bylander separable forms [17] without ghost bands. A partial core correction [18] is considered for the Ti and Mg pseudopotentials. The wave function is expanded in plane waves and the cutoff energy is 36 Ry. The mesh sizes of the sampling k-points in the whole Brillouin zone (BZ) are 2x2x1 (= 4). The band gap values of TiN dot/MgO-4x4 and 5x5 superlattices which were relaxed in the 2x2x1 k-point mesh are obtained in the 4x4x1 (=16) k-point mesh. All atoms in the supercell were fully relaxed. In this study, two TiN dot structures are considered. One is one Ti and one N atoms per layer as a rectangular shape and the other is two Ti and two N atoms per layer as a rectangular parallelepiped shape as shown in Fig. 1, schematically. A layer number of each dot structure is two.

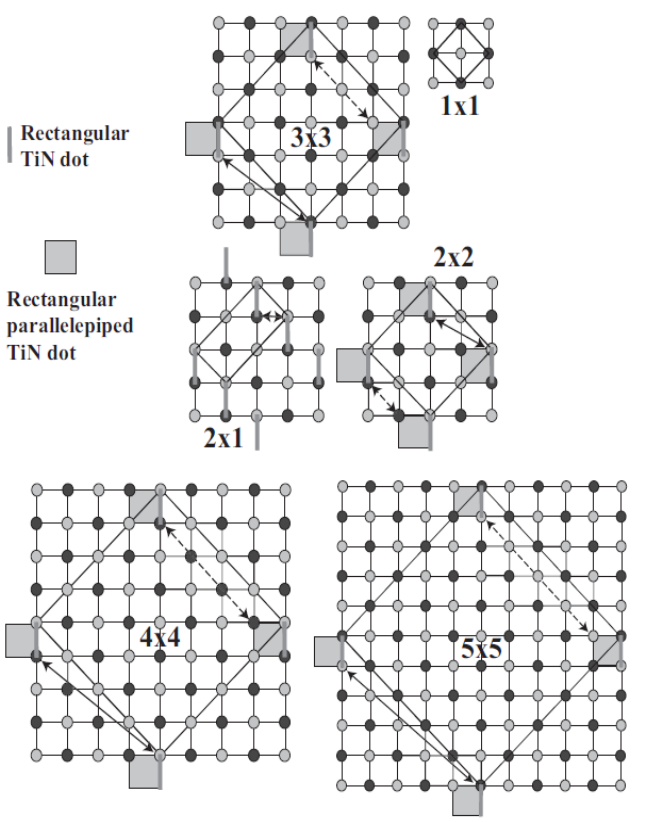

Fig. 1 Top view of TiN/MgO-1x1, 2x1, 2x2, 3x3, 4x4, and 5x5 superlattices. The 4x4 and 5x5 superlattice are investigated in the present study. Shaded stick and rectangular indicate “rectangular TiN dot” and “rectangular parallelepiped TiN dot”, respectively. The number of atoms in the supercells for the rectangular (rectangular

parallelepiped) TiN dot/MgO-4x4 and 5x5 superlattices are 132 (136) and 204 (208), respectively. The layer numbers of the MgO substrate (4x4 and 5x5) and vacuum region are four and six, respectively. Solid and dotted leftrightarrows indicate the nearest neighbor distances of rectangular and rectangular parallelepiped TiN dots, respectively.

Table I Band gap values of TiN/MgO superlattices. "R" and "RP" indicate the rectangular and rectangular parallelepiped TiN dots, respectively.

Superlattice	Shape	Number of k-points	Band gap (eV)
TiN/MgO-2x2	R	16	0.18
TiN/MgO-2x2	RP	16	-
TiN/MgO-3x3	R	36	0.54
TiN/MgO-3x3	RP	16	-
TiN/MgO-4x4	R	16	0.57
TiN/MgO-4x4	RP	16	0.29
TiN/MgO-5x5	R	16	0.58
TiN/MgO-5x5	RP	16	0.17

3. Results and Discussion

As a result of calculations, the rectangular TiN dot/MgO-4x4 and 5x5 superlattices correspond to semiconductor. The rectangular parallelepiped TiN dot/MgO-4x4 and 5x5 superlattices also correspond to semiconductor although those of 2x2 and 3x3 superlattices correspond to metallicity. It will be expected that the band gap value of the TiN dot/MgO-5x5 superlattice is larger than that of the TiN dot/MgO-4x4 superlattice because the band gap of MgO (bulk) is quite large with 4.60 eV (7.67 eV) in LDA (experiment [19]).

The band gap values in the TiN dot/MgO-4x4 and 5x5 superlattices are tabulated in Table I. Previous results of the TiN dot/MgO-2x2 and 3x3 superlattices are also tabulated in Table I in order to compare with the present results. The band gap values of the rectangular TiN dot/MgO superlattices are larger than those of the rectangular parallelepiped TiN dot/MgO superlattices, although it could be underestimated them due to inaccuracy of the DFT-LDA calculation. As for the rectangular dot, the band gap value increases with increasing the size of the MgO substrate. In contrast, the band gap value of the rectangular parallelepiped TiN/MgO-5x5 is smaller than that of the rectangular parallelepiped TiN/MgO-4x4. It is obvious that the electronic state of the TiN dot/MgO superlattice depends on its dot shape and the size of MgO substrate. The band gap value of the TiN dot/MgO superlattice could be controllable to vary its TiN dot shape and MgO substrate size.

4. Conclusions

We have calculated the internal lattice and electronic properties of rectangular and rectangular parallelepiped TiN dot/MgO-4x4 and 5x5 superlattices using the total energy pseudopotential method. The electronic properties of the various TiN dot/MgO superlattices (2x2 – 5x5) have been definitively established in the present and previous studies. The electronic structures of all rectangular TiN dot/MgO superlattices (2x2 – 5x5) are semiconducting. The rectangular parallelepiped TiN dot/MgO-4x4 and 5x5 superlattices also correspond to semiconductor. The maximum band gap value is 0.58 eV (rectangular, 5x5). It is found that the TiN dot shape and MgO substrate size are important to control the band gap value.

Acknowledgements

We would like to extend our thanks to Dr. T. Mori of NIMS for continual support. This study is supported by JST CREST Grant Number JPMJCR15Q6, Japan. The numerical calculations were performed using Z420, Z440, Z620, and Z640 workstations (HP), and the numerical materials simulator [Altix, SGI] in NIMS.

References

[1] K. Kobayashi, N. Kobayashi, and K. Hirose, *e-J. Surf. Sci. Nanotech.*, **12** (2014) 230.

[2] K. Kobayashi, H. Takaki, N. Kobayashi, and K. Hirose, JPS Conf. Proc. **5** (2015) 011013.

[3] K. Kobayashi, H. Takaki, M. Shimono, N. Kobayashi, and K. Hirose, Jpn. J. Appl. Phys. **56** (2017) 04CK06.

[4] I. Ohkubo, T. Aizawa, and T. Mori, private communications.

[5] L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B**47** (1993) 12727.

[6] L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B**47** (1993) 16631.

[7] J. O. Sofo and G. D. Mahan, Appl. Phys. Lett. **65** (1994) 2690.

[8] A. J. Minnich, M. S. Dresselhaus, Z. F. Ren, and G. Chen, Energy Environ. Sci. **2** (2009) 466.

[9] K. Hirose, K. Kobayashi, M. Shimono, H. Ishii, and N. Kobayashi, *e-J. Surf. Sci. Nanotech.*, **12** (2014) 115.

[10] H. Takaki, K. Kobayashi, M. Shimono, N. Kobayashi, and K. Hirose, J. Appl. Phys. **119** (2016) 014302.

[11] H. Takaki, K. Kobayashi, M. Shimono, N. Kobayashi, and K. Hirose, J. Electron. Mater. **46** (2017) 5593.

[12] P. Hohenberg and W. Kohn, Phys. Rev. **136** (1964) B864.

[13] W. Kohn and L. J. Sham, Phys. Rev. **140** (1965) A1133.

[14] E. P. Wigner: Phys. Rev. **46** (1934) 1002.

[15] N. Troullier and J. L. Martins: Phys. Rev. B **43** (1991) 1993.

[16] K. Kobayashi, Mater. Trans. **42** (2001) 2153.

[17] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48** (1982) 1425.

[18] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26** (1982) 1738.

[19] W. Martienssen and H. Warlimont 2005 *Springer Handbook of Condensed Matter and Materials Data* (Heidelberg: Springer) 656.