Fabrication of noncentrosymmetric Nb/V/Ta superlattice and its superconductivity

F. Ando¹, D. Kan¹, Y. Shiota¹, T. Moriyama¹, Y. Shimakawa^{1,2}, and T. Ono^{1,3}

¹Institute for Chemical Research, Kyoto University, *Gokasho Uji, Kyoto 611-0011, Japan*

²Integrated Research Consortium on Chemical Sciences, Kyoto University, *Gokasho Uji, Kyoto 611-0011, Japan*

³Center for Spintronics Research Network (CSRN), Graduate School of Engineering Science, Osaka University, *1-3 Machikaneyama-cho Toyonaka, Osaka 560-8531, Japan*

Nb, V, and Ta are all well-known superconducting elements in a simple substance. We report the superconductivity of Nb/V/Ta superlattices sputtered onto MgO(100) substrates, in which global inversion symmetry was broken along the stacking direction. It was found that the superlattices had long-range crystalline coherence with the well-defined periodicity of the constituent layers, and they exhibited superconducting transition despite the thicknesses of the layers.

Keywords: inversion symmetry breaking, artificial superlattice, epitaxial film, X-ray $2\theta/\theta$ measurement, superconductivity

1. Introduction

In recent years, spin-orbit interaction (SOI) has been attracted intense attentions in the various fields of solid state physics, such as spintronics^{1)–3)}, topological matter⁴⁾, and unconventional superconductivity⁵⁾. In the presence of inversion symmetry breaking, SOI entangles the spin and orbit degrees of freedom in the electron system and enables the mutual control of electronic and spin properties. In case of superconductors, the SOI with broken inversion symmetry significantly forbids the conventional classification of Cooper pairs⁶⁾. Instead, a new pairing symmetry, i.e., a mixed spin singlet-triplet state, is expected to be realized^{6),7)}. There have been several reports of the noncentrosymmetric superconductors where the crystal structure lacks a center of inversion, such as CePt₃Si⁸⁾, CeRhSi₃^{9),10)}, and UIr¹¹⁾.

Recently, Rashba effect on two-dimensional (2D) superconductivity was studied using d-wave heavy fermion superconductor CeCoIn₅ sandwiched by two different nonmagnetic metals¹²⁾. This previous work reveals that Rashba effect controlled in the tricolor structure exerts profound changes in the 2D superconducting properties as theoretically pointed out^{13),14)}. The finding naturally leads us to an expectation that an exotic superconductivity can be explored in 3D artificially engineered superlattice using three kinds of superconductors A, B, and C. As shown in Fig. 1(a), global inversion symmetry is broken in *ABC*-type superlattice and we can easily tune Rashba effect yielded by asymmetric potential gradient ∇V .

In this study, we at first investigate the growth and conductivity of *ABC*-type superlattices as a new platform to investigate an exotic superconductivity. We choose Nb, V, and Ta as the constituent layers, which are all commonly-used superconducting elements and have body-centered cubic (bcc) lattice structure^{15)–19)}.

2. Experimental Procedure

The film deposition was carried out by d.c. magnetron sputtering in an high vacuum system at a base pressure of 1.0×10^{-5} Pa or better. Ar was used as sputter gas. Prior to film growth, the MgO(100) substrate was washed with acetone and heated at 600 °C for 30 minutes in the sputtering chamber to drive off impurities. Figure 1(b) shows a design of the superlattice structure. Nb, V, and Ta layers of the thickness t were repetitively sputtered onto the MgO substrate. The deposition rates were kept constant at 0.35, 0.21, and 0.44 Å/s for Nb, V, and Ta, respectively. The MgO substrate was heated at 750 °C during the deposition as well as the previous report¹⁷⁾. We changed the thickness t from 1.0 nm to 5.0 nm while fixing the total thickness to be 60 nm. We can expect that Rashba effect on the superconductivity can be controlled by tuning the thickness t . A 3 nm thick Pt layer deposited at room temperature prevents the oxidation.

To confirm the epitaxial growth of Nb/V/Ta superlattices, reflection high-energy electron diffraction (RHEED) patterns were observed *in-situ* before and after the deposition of the superlattices. The electron beam was injected along the MgO[100] and MgO[110] azimuthal directions. Figure 1(b) shows the RHEED patterns of MgO substrate (1st) and Nb/V/Ta superlattice for $t = 1.0$ nm (2nd). The observed patterns indicate an epitaxial growth of the bcc-Nb/V/Ta superlattice with Nb/V/Ta(100) on the MgO(100) substrate where Nb/V/Ta[100]||MgO[100]^{20),21)}. The in-plane lattice constant of the top Ta surface is estimated to be 3.2 Å from the RHEED streak distance²²⁾. This smaller lattice constant compared with that of bulk bcc-Ta (3.30 Å) can be accounted for by a lattice mismatch with the neighboring V layer. The similar RHEED patterns were observed for other films ($t = 2.0$ and 5.0 nm, [Nb (2.0)/V (2.0)/Ta (2.0)] $\times 10$ and [Nb (5.0)/V (5.0)/Ta (5.0)] $\times 4$).

Fig. 1 (a) Schematic design of *ABC*-type superlattice. Red arrow represents asymmetric potential gradient ∇V due to global inversion symmetry breaking. (b) Film structure sputtered onto MgO (100) substrates. Nb, V, and Ta were chosen as constituent elements for *ABC*-type superlattice. RHEED streak patterns were observed before and after deposition of $[\text{Nb} (1.0)/\text{V} (1.0)/\text{Ta} (1.0)]_{20}$ superlattice. Electron beam was injected along the MgO[100] and MgO[110] azimuthal directions.

Fig. 2 X-ray $2\theta/\theta$ measurements for $[\text{Nb} (1.0)/\text{V} (1.0)/\text{Ta} (1.0)]_{20}/\text{Pt} (3.0)$. (a) Measured (red) and calculated (blue) X-ray reflection curves identify interfacial morphology of superlattice. Two distinct fringes resulting from interference between periodic interfaces indicate highly sharp interfaces with almost no mixture. (b) X-ray diffraction scan was performed to identify crystalline structure of superlattice. Two sharp peaks corresponding to MgO(200) and Nb(200) [or Ta(200)] strongly indicate that superlattice was epitaxially grown with bcc lattice structure on MgO(100) substrate.

3. Results and Discussions

To investigate the interfacial morphology and crystalline structure of the superlattice, we performed X-ray $2\theta/\theta$ measurements²³⁾ using Philips X'Pert MRD diffractometer with monochromatic $\text{CuK}\alpha_1$ radiation. Figure 2(a) shows the measured and calculated X-ray reflection curves of the superlattice ($t = 1.0$ nm). The measured curve shows two noticeable Bragg peaks and Kiessig fringes²⁴⁾. From the series of the two peak-angles, it is directly found that the film has a characteristic length of 2.84 nm. This means that the 2.8-nm-thick Nb/V/Ta multi-layers are periodically deposited with highly sharp interfaces, which is a desirable construction to enhance Rashba effect. The measured curve was fitted as a function of thicknesses and roughness of Nb, V, and Ta layers using a Philips X'Pert reflectivity program. The calculated curve clearly reproduces two Bragg peaks and

Kiessig fringes of the measured one. The calculated thicknesses of Nb, V, and Ta layers are 0.9, 1.0, and 0.9 nm, respectively, which almost agree with the original design of the superlattice. Mean values of the interfacial roughness obtained from the fit were equal to 0.4-0.9 nm (2-4 atomic layers).

Secondly, we performed the X-ray diffraction (XRD) scan for the same film ($t = 1.0$ nm). Figure 2(b) shows the obtained result of XRD scan. The expected angles of the peaks are calculated using lattice constants listed in the *American Institute of Physics Handbook*²²⁾. A distinct peak around 56° can be seen in the measured XRD curve, which corresponds to the expected one from bcc-Nb(200) or bcc-Ta(200). Together with the RHEED 2nd in Fig. 1(b), the XRD curve ensures the epitaxial growth of the deposited films with bcc lattice structure.

Finally, we conducted electric transport measurements to characterize the electrical conductivity at low

Fig. 3 Temperature dependence of electric resistivity in Nb/V/Ta superlattices ($t = 1.0$, 2.0 , and 5.0 nm) and 120 -nm-thick Nb, V, Ta single-layer films. Inset shows photomicrograph of processed film along with measurement configuration. All [Nb/V/Ta] superlattices exhibited abrupt drop in resistivity.

temperature. In order to enhance the 3D nature^{25),26)}, we fabricated the superlattices increasing the total thickness from 60 nm to 120 nm. Note that there is almost no difference in RHEED patterns by increasing the total thickness. The inset of Fig. 3(a) shows a photomicrograph of the processed film with the measurement configuration. The films were patterned into a 50 - μm -wide wire structure by a conventional photolithography and Ar ion milling process. Then, Cr (5 nm)/Au (100 nm) electrodes were formed on the films using a resistance heating evaporation system and a lift-off process. Four-terminal measurements were performed to probe the temperature dependence of the sheet resistivity using the Physical Property Measurement System (PPMS-9T, Quantum Design). Figure 3(a) shows the measurement results for the superlattices ($t = 1.0$, 2.0 , 5.0 nm) with those for 120 -nm-thick Nb, V, Ta single layer films. The superlattices exhibit the superconducting transitions, whose temperatures T_c are comparable to those of Nb, V, Ta single layer films. However, the t dependence of the T_c is somehow strange because T_c among the superlattice ($t = 2.0$ nm) is the highest of the three films. We need further study about the physics behind the superconductivity.

4. Conclusion

We study the growth and superconductivity of Nb/V/Ta superlattices sputtered onto MgO(100) substrates. The RHEED patterns and X-ray $2\theta/\theta$ measurements reveal that the superlattices have long-range crystalline coherence and the well-defined periodicity of the constituent layers. Moreover, the superlattices exhibited superconducting transition comparable to the Nb, V, and Ta single layer films. The ABC-type noncentrosymmetric superlattice presented in this work will be a new platform for searching exotic superconductive

properties^{7),10),27)–30)}.

Acknowledgements This work was supported by JSPS KAKENHI Grant Numbers 15H05702, 16H05977, 26103002, the Collaborative Research Program of the Institute for Chemical Research, Kyoto University, and the Cooperative Research Project Program of the Research Institute of Electrical Communication, Tohoku University.

References

- 1) S. Murakami, N. Nagaosa, and S. Zhang, *Science* **301**, 1348 (2003).
- 2) J. Sinova, D. Culcer, Q. Niu, N.A. Sinitsyn, T. Jungwirth, and A.H. MacDonald, *Phys. Rev. Lett.* **92**, 126603 (2004).
- 3) A. Fert, V. Cros, and J. Sampaio, *Nat. Nanotechnol.* **8**, 152 (2013).
- 4) X. Qi and S. Zhang, *Rev. Mod. Phys.* **83**, 1057 (2011).
- 5) E. Bauer and M. Sigrist, *Non-Centrosymmetric Superconductors: Introduction and Overview* (Springer-Verlag Berlin Heidelberg, 2012).
- 6) L.P. Gor'kov and E.I. Rashba, *Phys. Rev. Lett.* **87**, 37004 (2001).
- 7) P. Frigeri, D.F. Agterberg, A. Koga, and M. Sigrist, *Phys. Rev. Lett.* **92**, 097001 (2004).
- 8) E. Bauer, G. Hilscher, H. Michor, C. Paul, E.W. Scheidt, A. Griбанov, Y. Seropegin, H. Noël, M. Sigrist, and P. Rogl, *Phys. Rev. Lett.* **92**, 027003 (2004).
- 9) N. Kimura, K. Ito, K. Saitoh, Y. Umeda, H. Aoki, and T. Terashima, *Phys. Rev. Lett.* **95**, 247004 (2005).
- 10) N. Kimura, K. Ito, H. Aoki, S. Uji, and T. Terashima, *Phys. Rev. Lett.* **98**, 197001 (2007).
- 11) T. Akazawa, H. Hidaka, T. Fujiwara, T.C. Kobayashi, E. Yamamoto, Y. Haga, R. Settai, and Y. Onuki, *J. Phys. Condens. Matter* **16**, L29 (2004).
- 12) M. Naritsuka, T. Ishii, S. Miyake, Y. Tokiwa, R. Toda, M. Shimozaawa, T. Terashima, T. Shibauchi, Y. Matsuda, and Y. Kasahara, *Phys. Rev. B* **96**, 174512 (2017).
- 13) S. Fujimoto, *J. Phys. Soc. Jpn.* **76**, 051008 (2007).
- 14) D. Maruyama and Y. Yanase, *J. Phys. Soc. Jpn.* **84**, 074702 (2015).
- 15) B.Y. Jin and J.B. Ketterson, *Adv. Phys.* **38**, 189 (1989).
- 16) J.R. Rairden and C.A. Neugebauer, *Proc. IEEE* **52**, 1234 (1964).
- 17) S.M. Durbin, J.E. Cunningham, M.E. Mochel, and C.P. Flynn, *J. Phys. F Met. Phys.* **11**, L223 (1981).
- 18) P.R. Broussard and T.H. Geballe, *Phys. Rev. B* **35**, 1664 (1987).
- 19) M. Gutsche, H. Kraus, J. Jochum, B. Kemmather, and G. Gutekunst, *Thin Solid Films* **248**, 18 (1994).
- 20) D.B. Beringer, W.M. Roach, C. Clavero, C.E. Reece, and R.A. Lukaszew, *Phys. Rev. ST Accel. Beams* **16**, 022001 (2013).
- 21) G. Oya, M. Koishi, Y. Sawada, G. Oya, M. Koishi, and Y. Sawada, *J. Appl. Phys.* **60**, 1440 (1986).
- 22) D.E. Gray, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957).

- 23) W.J. Bartels, J. Hornstra, and D.J.W. Lobeek, in *Acta Crystallogr. Sect. A* (1986), pp. 409–588.
- 24) H. Zabel, *Appl. Phys. A* **58**, 159 (1994).
- 25) J.I. Kodama, M. Itoh, and H. Hirai, *J. Appl. Phys.* **54**, 4050 (1983).
- 26) A.I. Gubin, K.S. Il'in, S.A. Vitusevich, M. Siegel, and N. Klein, *Phys. Rev. B* **72**, 064503 (2005).
- 27) V.P. Mineev, *Low Temp. Phys.* **37**, 1092 (2011).
- 28) C. Lu and S. Yip, *Phys. Rev. B* **78**, 132502 (2008).
- 29) Y. Tanaka, T. Yokoyama, A. V Balatsky, and N. Nagaosa, *Phys. Rev. B* **79**, 060505(R) (2009).
- 30) M. Sato and S. Fujimoto, *Phys. Rev. Lett.* **105**, 217001 (2010).

Received Nov. 13, 2018; Accepted Jan. 21, 2019